Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The molecular and supramolecular structures of four 1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazolines

John Nicolson Low,[a]* Justo Cobo,[b] Manuel Nogueras,[b] Adolfo Sánchez,[b] Harlen Torres[c] and Braulio Insuasty[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad del Valle, AA25360 Cali, Colombia
Correspondence e-mail: jnlow111@hotmail.com

Received 3 April 2002
Accepted 8 April 2002
Online 30 April 2002

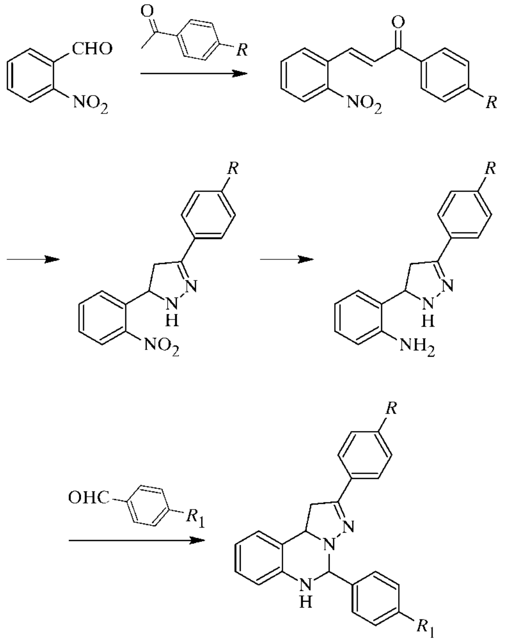
The supramolecular structures of the title compounds, 2-phenyl-5-*p*-tolyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, $C_{23}H_{21}N_3$, (I), 5-(4-bromophenyl)-2-phenyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, $C_{22}H_{18}BrN_3$, (II), 2-(4-chlorophenyl)-5-phenyl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, $C_{22}H_{18}ClN_3$, (III), and 5-(4-bromophenyl)-2-(4-chlorophenyl)-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazoline, $C_{22}H_{17}BrClN_3$, (IV), are of two general types. Compounds (I), (II) and (III) form base-paired dimers *via* N—H···N hydrogen bonds, where (I) and (II) are isomorphous, while in (IV), there are no conventional hydrogen bonds.

Comment

The quinazoline skeleton is an important pharmacophore that occurs frequently in the medicinal chemistry literature (Fry *et al.*, 1994). Pyrazolo[1,5-*c*]quinazolinones have been shown to be potent amino acid antagonists (McQuaid *et al.*, 1992), anti-inflammatory agents, immunosuppressants, and antiasthmatic and antiallergenic agents (Casey *et al.*, 1980).

We report herein the syntheses and crystal structures of four 2,5-diaryl-1,5,6,10b-tetrahydropyrazolo[1,5-*c*]quinazolines (see *Scheme*). The syntheses of these compounds were achieved in a four-step sequence, starting with a known condensation of *o*-nitrobenzaldehyde with the corresponding acetophenone, followed by reaction with hydrazine to afford the pyrazole ring formation, then reduction of the nitro group to amino, and finally a new cyclocondensation with different benzaldehydes to yield the desired compounds. Compounds (I), (II) and (IV) crystallize in the triclinic space group $P\bar{1}$, and (III) crystallizes in the monoclinic space group $C2/c$.

In the molecular structure of (IV), the arene ring attached to C2 is disordered over two sites, each with 50% site occupancy. The indications are that this is a correlated disorder. In all four compounds, the bonds and angles of the tricyclic moiety are similar, and identical within experimental error for the isomorphous compounds (I) and (II) (Tables 1, 3, 5 and 7; Figs. 1–4). The pyrazole rings are C10b-envelopes and the tetrahydropyrimidine rings have half-chair conformations (Cremer & Pople, 1975). The conformations of the arene substituents are very similar in compounds (I), (II) and (III), with, for example, the N3—C2—C21—C22 torsion angles being −177.79 (16), −178.0 (3) and 179.85 (15)°, respectively, and the N4—C5—C51—C52 angles 35.3 (2), 34.4(3) and 32.66 (18)°, respectively. In (IV), the arene ring defined by



	R	*R*1
(I)	H	Me
(II)	H	Br
(III)	Cl	H
(IV)	Cl	Br

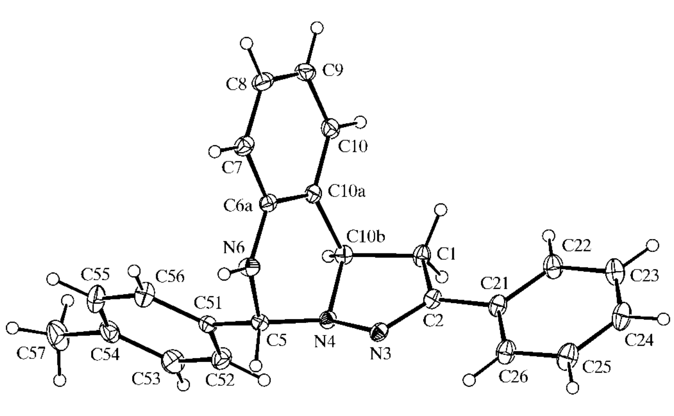


Figure 1
A view of the molecule of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

atoms C21–C26 is disordered and the N4—C5—C51—C52 torsion angle is 52.3 (2)°. These and related torsion angles are detailed in Tables 1, 3, 5 and 7.

In compounds (I)–(III), the molecules form $R^2_2(10)$ base-paired rings (Bernstein *et al.*, 1995); the H6···N3 distances are 2.26, 2.25 and 2.20 Å for (I), (II) and (III), respectively, the N6···N3 distances are 3.122 (2), 3.105 (3) and 3.083 (2) Å, respectively, and the angles at H6 are 164, 162 and 178°, respectively, with atom N3 being in the molecule at $(-x, 1-y, 1-z)$ for (I) and (II), and in that at $(\frac{3}{2}-x, \frac{1}{2}-y, 1-z)$ for (III) (Tables 2, 4 and 6). Fig. 5 displays this base-paired ring for (II) as an example.

What is unexpected, however, despite the close conformational similarities of the tricyclic moieties in the four structures, is that (IV) does not form an N6···N3 hydrogen bond. Instead, there is an N—H···π(arene) interaction involving the N6—H6 group and the C51–C56 arene ring at $(x-1, y, z)$, with a perpendicular distance of 2.57 Å from atom H6 to the ring (Table 8). This interaction links the molecules in chains along the *a* axis (Fig. 6). In addition, there is a short intermolecular C10b—H10*B*···N6$(x+1, y, z)$ contact, with H···N 2.52 Å, C···N 3.500 (3) Å and an angle at H of 168°. This seems to be adventitious and in conjunction with the N—H···π contact, as the contacts around atom N6 are not close to being tetrahedral; H10*B*$(x-1, y, z)$···N6—H6 is 155°, H10*B*$(x-1, y, z)$···N6—C6a is 63° and H10*B*$(x-1, y, z)$···N6—C7 is 92°.

In compounds (I) and (II), there is an intermolecular C—H···π(arene) interaction involving the C53—H53 group and the C21–C26 arene ring [centroid *Cg*4 at $(x, 1+y, z)$, Tables 2 and 4]. These link the molecules into a chain which runs along the *b* axis; Fig. 7 shows this chain for (II). In compound (III), there are two such interactions between C1—H1*A* and the C6a–C10a ring (centroid *Cg*3), and between C22—H22 and

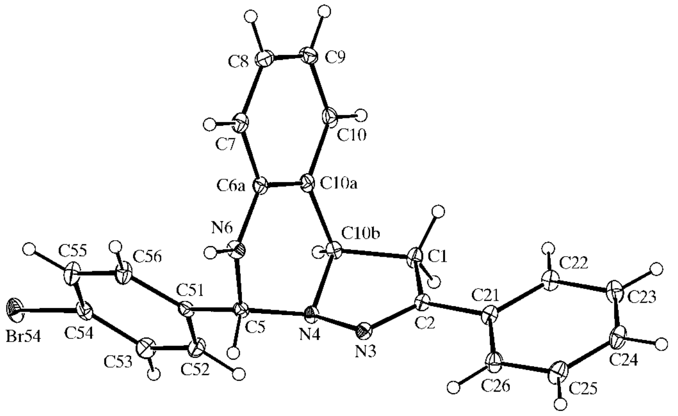


Figure 2
A view of the molecule of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

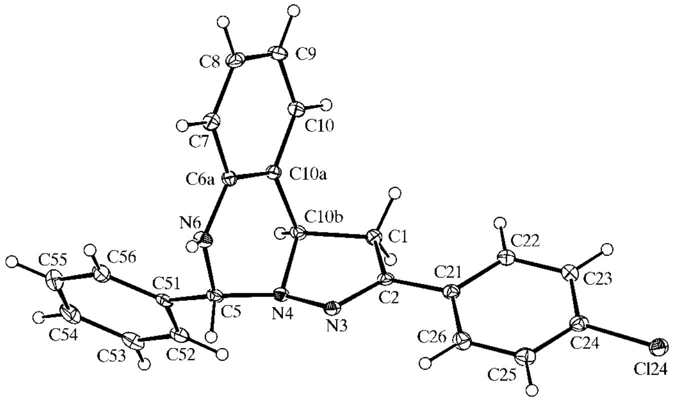


Figure 3
A view of the molecule of (III) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

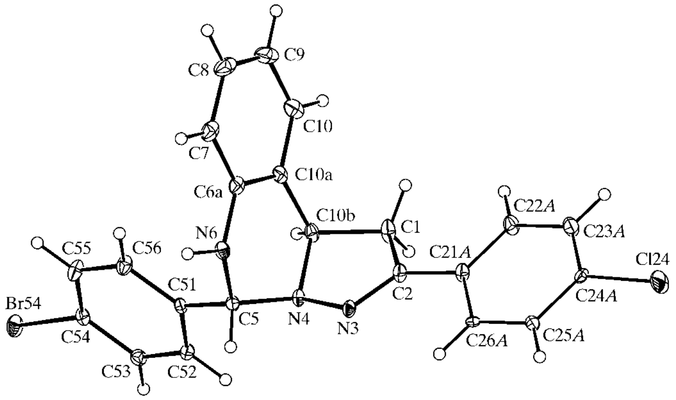


Figure 4
A view of the molecule of (IV) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor component of the disordered arene ring has been omitted.

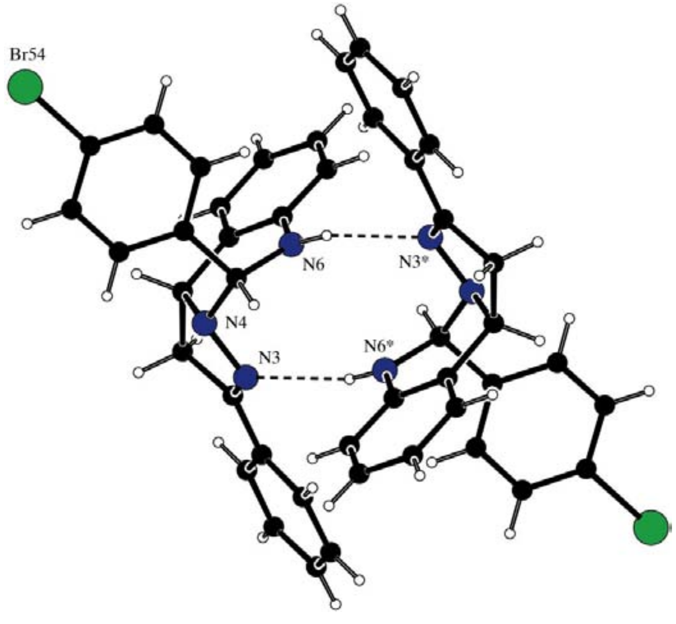


Figure 5
A view of the $R^2_2(10)$ ring structure in (II), which is similar to those found in (I) and (III). Atoms labelled with an asterisk (*) are at symmetry position $(-x, 1-y, 1-z)$.

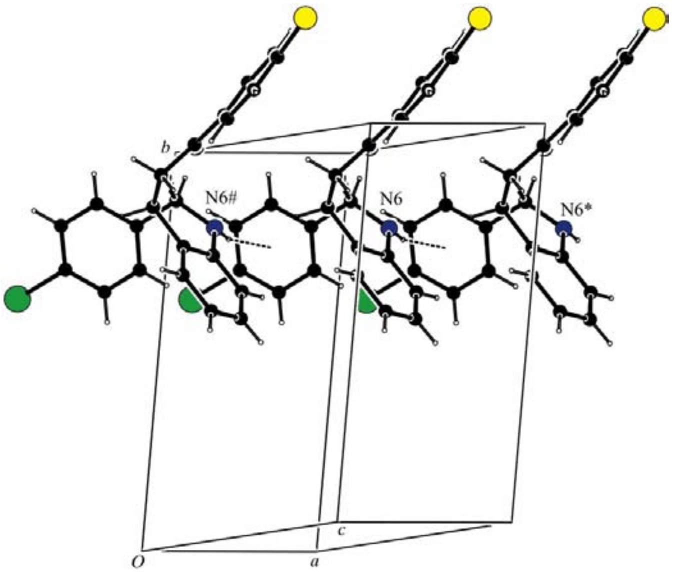


Figure 6
A view of the N—H$\cdots\pi$(arene) interaction involving the N6—H6 group and the C51–C56 ring in (IV), linking molecules along the *a* axis. Atoms labelled with an asterisk (*) or hash sign (#) are at symmetry positions ($x + 1, y, z$) and ($x - 1, y, z$), respectively.

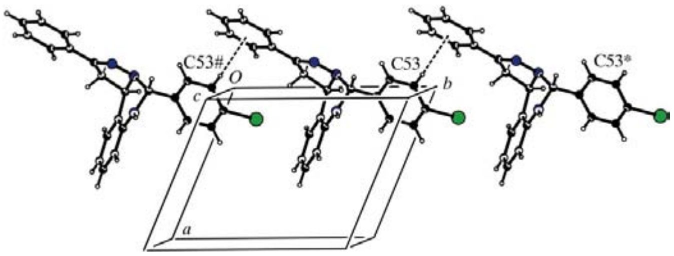


Figure 7
A view of the chain along the *b* axis formed by the C—H$\cdots\pi$(arene) interaction between the C53—H53 group and the C21–C26 ring in (II). The atom labelled with an asterisk (*) is in the molecule at ($x, 1 + y, z$) and that labelled with a hash sign (#) is in the molecule at ($x, 1 - y, z$).

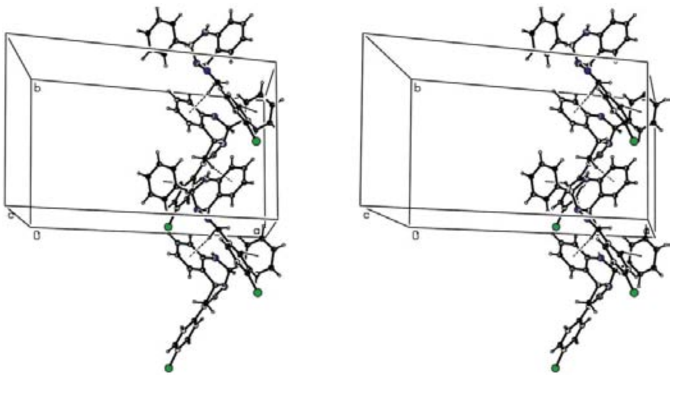


Figure 8
A stereoview of the spiral chain formed by C1*A*—H1*A*$\cdots\pi$(*Cg*3) and C22—H22$\cdots\pi$(*Cg*5) in (III); *Cg*3 is the centroid of the C6a/C7–C10/C10a ring and *Cg*5 is the centroid of the C51–C56 ring.

the C51–C56 ring (centroid *Cg*5); both these centroids are in the symmetry-related molecules at ($\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$). These interactions result in spiral chains formed by molecules related by the screw axis ($\frac{3}{4}, y, \frac{1}{4}$) and by symmetry-related screw axes. These chains run parallel to the *b* axis (Table 6 and Fig. 8). There is also a short intermolecular Cl24$\cdots$Cl24($2 - x, y, \frac{3}{2} - z$) contact in (III), with a Cl$\cdots$Cl distance of 3.4118 (6) Å.

There are no π–π-stacking interactions of significance in any of the four crystal structures. There is a potential solvent void of 35.6 Å^3 per unit-cell volume of 3508.8 Å^3 in (III), but there was no evidence of excess electron density in this volume. There are no solvent-accessible voids in the other three structures.

Experimental

For compounds (I)–(IV), a catalytic amount of acetic acid was added to an equimolar solution of the relevant dihydropyrazole starting material and aromatic aldehyde, and the resulting solutions stirred at room temperature for between 5 and 10 min. The resulting precipitates were filtered off and washed with fresh ethanol to yield white solids. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a dimethylformamide and ethyl acetate solution for (I), by diffusion using hexane and ethyl acetate solutions for (II) and (III), and by slow evaporation from an ethyl acetate solution for (IV). For (I), yield 86%, m.p. 486 K; analysis found: C 81.47, H 6.12, N 12.31%; calculated for $C_{23}H_{21}N_3$: C 81.38, H 6.24, N 12.38%. For (II), yield 92%, m.p. 536 K; analysis found: C 65.23, H 4.39, N 10.28%; calculated for $C_{22}H_{18}BrN_3$: C 65.36, H 4.49, N 10.39%. For (III), yield 81%, m.p. 507 K; analysis found: C 73.46, H 5.05, N 11.65%; calculated for $C_{22}H_{18}ClN_3$: C 73.43, H 5.04, N 11.68%. For (IV), yield 85%, m.p. 487 K; analysis found: C 60.19, H 3.81, N 9.48%; calculated for $C_{22}H_{17}BrClN_3$: C 60.23, H 3.91, N 9.58%.

Compound (I)

Crystal data

$C_{23}H_{21}N_3$
$M_r = 339.43$
Triclinic, $P\overline{1}$
$a = 8.5292$ (12) Å
$b = 10.7291$ (16) Å
$c = 11.0469$ (16) Å
$\alpha = 109.417$ (2)°
$\beta = 91.555$ (3)°
$\gamma = 110.945$ (3)°
$V = 878.1$ (2) Å^3
$Z = 2$
$D_x = 1.284$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3993 reflections
$\theta = 2.0$–29.1°
$\mu = 0.08$ mm^{-1}
$T = 120$ (1) K
Plate, colourless
0.18 × 0.08 × 0.04 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.986$, $T_{\max} = 0.997$
5532 measured reflections
3993 independent reflections
3451 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 29.1°$
$h = -11 \rightarrow 7$
$k = -13 \rightarrow 14$
$l = -12 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.146$
$S = 1.06$
3993 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0640P)^2 + 0.6107P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

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

C1—C2	1.512 (2)	N6—C6a	1.374 (2)
C1—C10b	1.539 (2)	C6a—C7	1.406 (2)
C2—N3	1.288 (2)	C6a—C10a	1.408 (2)
C2—C21	1.470 (2)	C7—C8	1.383 (2)
N3—N4	1.4147 (18)	C8—C9	1.384 (3)
N4—C5	1.4620 (19)	C9—C10	1.390 (3)
N4—C10b	1.483 (2)	C10—C10a	1.392 (2)
C5—N6	1.445 (2)	C10a—C10b	1.522 (2)
C2—C1—C10b	100.55 (12)	C8—C7—C6a	120.35 (16)
N3—C2—C1	112.68 (14)	C7—C8—C9	120.78 (16)
C2—N3—N4	108.49 (12)	C8—C9—C10	119.14 (16)
N3—N4—C5	112.26 (12)	C9—C10—C10a	121.52 (16)
N3—N4—C10b	107.96 (11)	C10—C10a—C6a	118.98 (15)
C5—N4—C10b	114.03 (12)	C10—C10a—C10b	120.53 (14)
N6—C5—N4	110.75 (12)	C6a—C10a—C10b	120.46 (13)
C6a—N6—C5	118.73 (13)	N4—C10b—C10a	112.68 (12)
N6—C6a—C7	120.66 (15)	N4—C10b—C1	100.43 (12)
N6—C6a—C10a	120.15 (14)	C10a—C10b—C1	112.68 (13)
C7—C6a—C10a	119.18 (15)		
N3—C2—C21—C22	−177.79 (16)	N6—C5—C51—C56	−24.1 (2)
C1—C2—C21—C22	5.8 (2)	N4—C5—C51—C56	−147.76 (16)
N3—C2—C21—C26	3.1 (3)	N6—C5—C51—C52	158.96 (15)
C1—C2—C21—C26	−173.30 (16)	N4—C5—C51—C52	35.3 (2)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

*Cg*4 is the centroid of the C21–C26 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···N3^{i}	0.88	2.26	3.122 (2)	164
C53—H53···*Cg*4^{ii}	0.95	2.75	3.635 (3)	156

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

Compound (II)

Crystal data

$C_{22}H_{18}BrN_3$
$M_r = 404.30$
Triclinic, $P\overline{1}$
$a = 8.5110$ (2) Å
$b = 10.7015$ (3) Å
$c = 11.0357$ (3) Å
$\alpha = 110.036$ (2)°
$\beta = 92.1613$ (15)°
$\gamma = 110.3276$ (10)°
$V = 871.37$ (4) Å^3

$Z = 2$
$D_x = 1.541$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3775 reflections
$\theta = 3.1$–27.5°
$\mu = 2.37$ mm^{-1}
$T = 120$ (1) K
Block, colourless
0.25 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.719$, $T_{\max} = 0.789$
12 439 measured reflections

3775 independent reflections
3235 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.091$
$S = 1.03$
3775 reflections
235 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.3379P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

C1—C2	1.511 (3)	C6a—C7	1.402 (3)
C1—C10b	1.537 (3)	C6a—C10a	1.407 (3)
C2—N3	1.288 (3)	C7—C8	1.389 (3)
N3—N4	1.416 (2)	C8—C9	1.382 (4)
N4—C5	1.465 (3)	C9—C10	1.388 (4)
N4—C10b	1.490 (3)	C10—C10a	1.392 (3)
C5—N6	1.440 (3)	C10a—C10b	1.519 (3)
N6—C6a	1.380 (3)		
C2—C1—C10b	101.04 (17)	C8—C7—C6a	120.0 (2)
N3—C2—C1	112.81 (18)	C9—C8—C7	120.6 (2)
C2—N3—N4	108.54 (17)	C8—C9—C10	119.4 (2)
N3—N4—C5	111.94 (17)	C9—C10—C10a	121.5 (2)
N3—N4—C10b	108.09 (16)	C10—C10a—C6a	118.7 (2)
C5—N4—C10b	114.10 (17)	C10—C10a—C10b	120.1 (2)
N6—C5—N4	111.18 (17)	C6a—C10a—C10b	121.17 (19)
C6a—N6—C5	118.43 (18)	N4—C10b—C10a	112.59 (17)
N6—C6a—C7	120.5 (2)	N4—C10b—C1	100.49 (16)
N6—C6a—C10a	119.8 (2)	C10a—C10b—C1	113.07 (18)
C7—C6a—C10a	119.7 (2)		
N3—C2—C21—C22	−178.0 (2)	N6—C5—C51—C56	−24.7 (3)
C1—C2—C21—C22	5.3 (3)	N4—C5—C51—C56	−148.6 (2)
N3—C2—C21—C26	3.0 (3)	N6—C5—C51—C52	158.4 (2)
C1—C2—C21—C26	−173.7 (2)	N4—C5—C51—C52	34.4 (3)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

*Cg*4 is the centroid of the C21–C26 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···N3^{i}	0.88	2.25	3.105 (3)	162
C53—H53···*Cg*4^{ii}	0.95	2.71	3.588 (3)	154

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

Compound (III)

Crystal data

$C_{22}H_{18}ClN_3$
$M_r = 359.84$
Monoclinic, $C2/c$
$a = 21.2115$ (3) Å
$b = 11.1385$ (2) Å
$c = 17.5948$ (4) Å
$\beta = 122.4270$ (10)°
$V = 3508.84$ (11) Å^3
$Z = 8$

$D_x = 1.362$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4002 reflections
$\theta = 3.0$–27.5°
$\mu = 0.23$ mm^{-1}
$T = 120$ (1) K
Block, colourless
0.46 × 0.32 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.902$, $T_{\max} = 0.978$
15 078 measured reflections

4002 independent reflections
3286 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\max} = 27.5°$
$h = -27 \rightarrow 27$
$k = -14 \rightarrow 13$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.01$
4002 reflections
235 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 2.7737P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

C1—C2	1.508 (2)	C6a—C7	1.401 (2)
C1—C10b	1.531 (2)	C6a—C10a	1.405 (2)
C2—N3	1.294 (2)	C7—C8	1.388 (2)
N3—N4	1.4079 (19)	C8—C9	1.388 (3)
N4—C5	1.457 (2)	C9—C10	1.384 (2)
N4—C10b	1.4804 (18)	C10—C10a	1.398 (2)
C5—N6	1.450 (2)	C10a—C10b	1.516 (2)
N6—C6a	1.3857 (19)		
C2—C1—C10b	100.69 (12)	C8—C7—C6a	120.46 (15)
N3—C2—C1	112.51 (14)	C9—C8—C7	120.72 (16)
C2—N3—N4	108.33 (12)	C10—C9—C8	118.82 (15)
N3—N4—C5	113.99 (12)	C9—C10—C10a	121.87 (16)
N3—N4—C10b	108.02 (11)	C10—C10a—C6a	118.90 (14)
C5—N4—C10b	114.96 (12)	C10—C10a—C10b	119.90 (14)
N6—C5—N4	112.34 (12)	C6a—C10a—C10b	121.16 (13)
C6a—N6—C5	119.01 (13)	N4—C10b—C10a	111.29 (12)
N6—C6a—C7	120.05 (14)	N4—C10b—C1	100.57 (12)
N6—C6a—C10a	120.74 (14)	C10a—C10b—C1	112.39 (12)
C7—C6a—C10a	119.21 (14)		
N3—C2—C21—C22	−179.85 (15)	N6—C5—C51—C56	−25.73 (19)
C1—C2—C21—C22	8.8 (2)	N4—C5—C51—C56	−150.49 (14)
N3—C2—C21—C26	4.5 (2)	N6—C5—C51—C52	157.43 (13)
C1—C2—C21—C26	−166.82 (15)	N4—C5—C51—C52	32.66 (18)

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

*Cg*3 and *Cg*5 are the centroids of the C6a/C7–C10/C10a and C51–C56 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···N3^{i}	0.88	2.20	3.083 (2)	178
C1—H1*A*···*Cg*3^{ii}	0.99	2.44	3.407 (2)	166
C22—H22···*Cg*5^{ii}	0.95	2.88	3.739 (2)	152

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

Compound (IV)

Crystal data

$C_{22}H_{17}BrClN_3$
$M_r = 438.75$
Triclinic, $P\overline{1}$
$a = 5.5560$ (1) Å
$b = 12.2526$ (2) Å
$c = 14.0827$ (3) Å
$\alpha = 77.9230$ (9)°
$\beta = 83.0060$ (8)°
$\gamma = 87.8140$ (10)°
$V = 930.41$ (3) Å^3

$Z = 2$
$D_x = 1.556$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4188 reflections
$\theta = 3.0$–27.4°
$\mu = 2.37$ mm^{-1}
$T = 120$ (1) K
Block, colourless
0.35 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.492$, $T_{\max} = 0.843$
14 350 measured reflections

4188 independent reflections
3683 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.068$
$\theta_{\max} = 27.4$°
$h = -7 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.080$
$S = 1.05$
4188 reflections
269 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.6775P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0130 (12)

Table 7
Selected geometric parameters (Å, °) for (IV).

C1—C2	1.510 (3)	N6—C6a	1.390 (3)
C1—C10b	1.534 (3)	C6a—C7	1.399 (3)
C2—N3	1.285 (3)	C6a—C10a	1.402 (3)
N3—N4	1.415 (2)	C7—C8	1.378 (4)
N4—C5	1.455 (3)	C8—C9	1.385 (4)
N4—C10b	1.488 (3)	C9—C10	1.387 (4)
C5—N6	1.450 (3)	C10—C10a	1.399 (3)
C5—C51	1.529 (3)	C10a—C10b	1.518 (3)
C2—C1—C10b	100.36 (16)	C8—C7—C6a	120.6 (2)
N3—C2—C1	112.92 (18)	C7—C8—C9	120.4 (2)
C2—N3—N4	108.33 (16)	C8—C9—C10	119.5 (2)
N3—N4—C5	111.42 (15)	C9—C10—C10a	121.3 (2)
N3—N4—C10b	107.92 (15)	C10—C10a—C6a	118.5 (2)
C5—N4—C10b	114.33 (16)	C10—C10a—C10b	120.60 (19)
N6—C5—N4	109.97 (16)	C6a—C10a—C10b	120.85 (18)
C6a—N6—C5	117.60 (16)	N4—C10b—C10a	112.50 (16)
N6—C6a—C7	120.4 (2)	N4—C10b—C1	100.20 (16)
N6—C6a—C10a	119.88 (19)	C10a—C10b—C1	112.66 (18)
C7—C6a—C10a	119.7 (2)		
N3—C2—C21*A*—C22*A*	−168.8 (3)	N6—C5—C51—C56	−7.4 (3)
N3—C2—C21*A*—C26*A*	14.1 (4)	N4—C5—C51—C56	−131.0 (2)
N3—C2—C21*B*—C22*B*	159.1 (2)	N6—C5—C51—C52	175.91 (17)
N3—C2—C21*B*—C26*B*	−25.1 (4)	N4—C5—C51—C52	52.3 (2)

Table 8
Hydrogen-bonding geometry (Å, °) for (IV).

*Cg*5 is the centroid of the C51–C56 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···*Cg*5^{i}	0.88	2.82	3.666 (2)	163
C10b—H10*B*···N6^{ii}	1.00	2.52	3.500 (3)	168

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

Compounds (I), (II) and (IV) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and confirmed by the analysis in each case. The disordered arene group in (IV) was modelled as two regular hexagons, each formed using the *SHELXL AFIX* 6 instruction and refined using the *PART* instruction (*SHELXL*97; Sheldrick, 1997). Refinement of a tied site-occupancy factor indicated an occupancy of 0.5 for each group. That this should be the case is indicated by the fact that, for the C21*A*–C26*A* group, there could be short intermolecular contacts in the range 2.72–3.11 Å to the group of atoms C22*A*–C24*A* in the molecule at ($1-x$, $-y$, $2-z$). Thus, there is correlated disorder of these arene groups, in which alternate arene groups interchange between conformations *A* and *B* for each centrosymmetric pair. An attempt was made to refine the structure in space group *P*1. The resulting refinement would not stabilize, with high oscillating shifts for atoms and large correlations between refined parameters. An attempt to split Cl54 into two discrete atoms was not successful. Compound (III) crystallized in the monoclinic system; space group *C*2/*c* or *Cc* was assumed from the systematic absences and *C*2/*c* was confirmed by the analysis. In compounds (I)–(IV), all H atoms were treated as riding atoms, with C—H = 0.95–1.00 Å and N—H = 0.88 Å.

For compound (I), data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997). For compounds (II), (III) and (IV), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*. For all compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton. The authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1111). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (1997). *SADABS*, *SMART* and *SHELXTL*. Versions 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Casey, F. B., Abboa-Offei, B. E. & Marretta, J. (1980). *J. Pharmacol. Exp. Ther.* **213**, 432–436.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Fry, D. W., Kraker, A. J., McMichael, A., Ambroso, L. A., Nelson, J. M., Leopold, W. R., Connors, R. W. & Bridges, A. L. (1994). *Science*, **265**, 1093–1095.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

McQuaid, L., Smith, E., South, K., Mitch, C. H., Schoepp, D., True, R., Calligaro, D., O'Malley, P., Lodge, D. & Ornstein, P. (1992). *J. Med. Chem.* **35**, 3319–3324.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2002). *PLATON*. University of Utrecht, The Netherlands.