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Supramolecular hydrogen-bonded hexamers in two 5-aryl-3-methyl-1-phenyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*][1,4]diazepines

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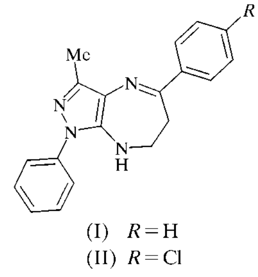
In both title compounds, *i.e.* 3-methyl-1,5-diphenyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*][1,4]diazepine, $C_{19}H_{18}N_4$, (I), and 5-(4-chlorophenyl)-3-methyl-1-phenyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*][1,4]diazepine, $C_{19}H_{17}ClN_4$, (II), an N—H···N hydrogen bond links six molecules to form an $R_6^6(30)$ ring. Compound (I) crystallizes in the $R\overline{3}$ space group and (II) crystallizes in $P\overline{1}$ with three molecules in the asymmetric unit. The molecule of (I) contains a disordered seven-membered ring.

Comment

Benzodiazepines are an important class of heterocyclic compounds used in psychotherapy. In recent years, analogous behaviour has been reported for other heterocyclic fused diazepine systems (Chimirri *et al.*, 1993; DeWald *et al.*, 1981; Sharp, 1984; Sternbach, 1978). We present here the crystal structure of two pyrazolodiazepines prepared by the reaction between 4,5-diaminopyrazole and 1-aryl-2-propenones (Insuasty *et al.*, 1999), namely 3-methyl-1,5-diphenyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*][1,4]diazepine, (I), and 5-(4-chlorophenyl)-3-methyl-1-phenyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*][1,4]diazepine, (II).



(I) $R=H$
(II) $R=Cl$

In (I), atoms C6 and C7 in the seven-membered ring are disordered, with the major component having a site-occupancy factor of 0.801. The torsion angles related to the major and minor components are given in Table 1. The deviations from the mean C5/N4/C3a/C8a/N8 plane are 0.534 (3) and

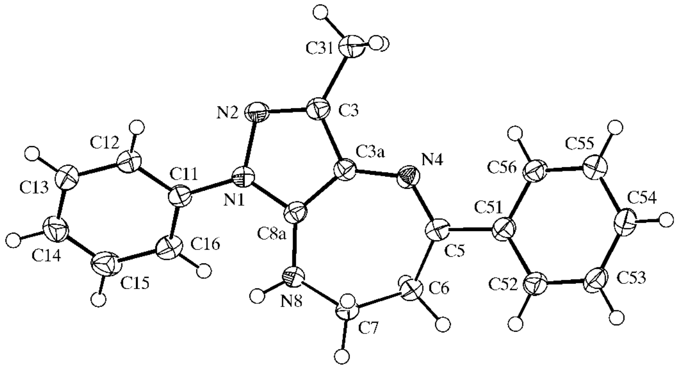


Figure 1
A view of the major component of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

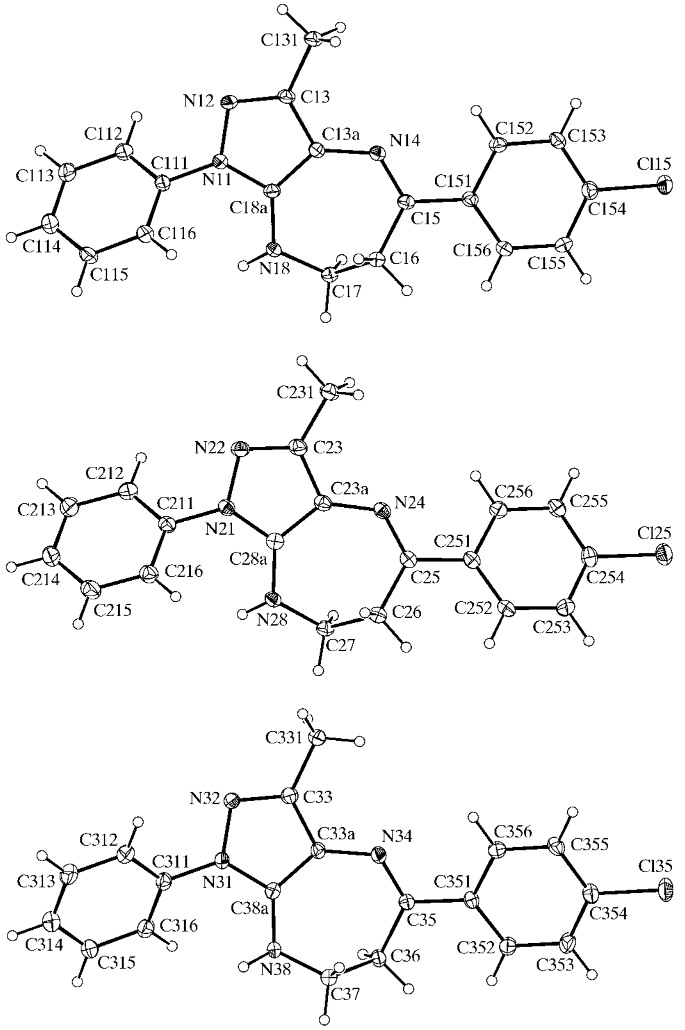


Figure 2
Views of the three molecules of the asymmetric unit of (II) with the atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level.

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−0.680 (8) Å for C6 and C61, respectively. The corresponding values for C7 and C71 are −0.372 (4) and 0.269 (12) Å, respectively. Thus, the twists are in the opposite directions for the major and minor components. Fig. 1 shows the major component.

The torsion angles for the seven-membered rings for the three molecules of (II) are given in Table 3. Views of the three molecules in the asymmetric unit are shown in Fig. 2.

In (I), the N—H···N hydrogen bond [N8—H8···N2($x - y$, x, $1 - z$)] in the structure, by action of the $\overline{3}$ symmetry axis, links six molecules to form a hexamer with an $R_6^6(30)$ ring (Bernstein *et al.*, 1995; Table 2 and Fig. 3). These rings are repeated at $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ by space-group symmetry. There are no other significant intermolecular contacts.

In (II), which crystallizes in the triclinic space group $P\overline{1}$, there are three molecules in the asymmetric unit which were selected such that the three molecules were linked to each other by an N*I*8—H*I*8···N*J*2 hydrogen bond (*I* and *J* denote the prefix numbers for the three molecules). The action of a centre of symmetry at $(0,\frac{1}{2},1)$ forms a hexamer with an identical $R_6^6(30)$ ring structure (Bernstein *et al.*, 1995) to (I) (Fig. 4).

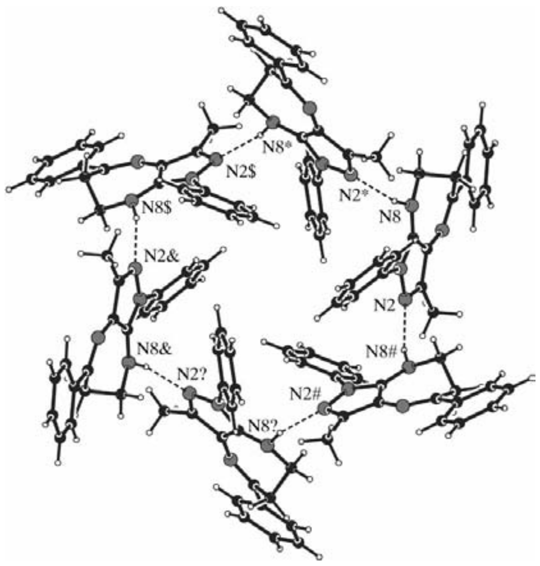

Figure 3
A view of the supramolecular structure of (I) showing the $R_6^6(30)$ ring. The molecules are at the following symmetry positions: ($) $-y$, $x - y$, z; (?) $-x + y$, $-x$, z; (&) $-x$, $-y$, $1 - z$; (#) y, $-x + y$, $-z$; (*) $x - y$, x, $-z$.

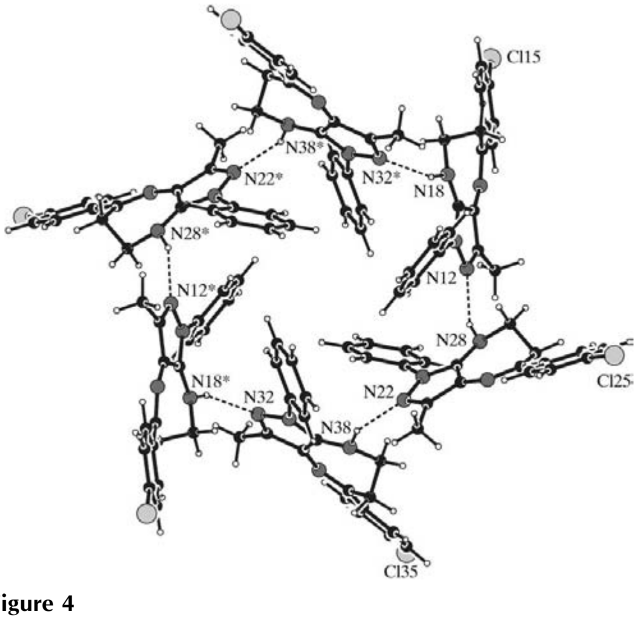

Figure 4
A view of the the supramolecular structure of (II) showing the $R_6^6(30)$ ring. The molecules labelled with an asterisk (*) are at the symmetry position ($-x$, $1 - y$, $2 - z$). The unit-cell box has been omitted for clarity.

Experimental

The title compounds were prepared as described previously by Insuasty *et al.* (1999).

Compound (I)

Crystal data

$C_{19}H_{18}N_4$
$M_r = 302.38$
Trigonal, $R\overline{3}$
$a = 30.5212$ (7) Å
$c = 8.8689$ (2) Å
$V = 7154.9$ (3) Å^3
$Z = 18$
$D_x = 1.263$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3272 reflections
$\theta = 3.1$–27.1°
$\mu = 0.08$ mm^{-1}
$T = 120$ (1) K
Plate, yellow
0.25 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.981$, $T_{\max} = 0.992$
40 810 measured reflections
3272 independent reflections
2600 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 27.1°$
$h = -32 \rightarrow 38$
$k = -39 \rightarrow 20$
$l = -8 \rightarrow 11$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.133$
$S = 1.05$
3272 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 6.7105P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

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

C8a—C3a—N4—C5	12.6 (3)	C5—C61—C71—N8	−94.3 (9)
C3a—N4—C5—C6	11.4 (3)	C6—C7—N8—C8a	−53.5 (3)
N4—C5—C6—C7	−61.5 (2)	C71—N8—C8a—C3a	−15.5 (5)
C61—C5—C6—C7	28.7 (5)	C7—N8—C8a—C3a	13.0 (3)
C5—C6—C7—N8	84.6 (2)	N4—C3a—C8a—N8	−3.2 (3)
N4—C5—C61—C71	83.8 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8···N2$^{\rm i}$	0.88	2.12	2.963 (2)	160

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

Table 3
Selected torsion angles (°) for (II).

C18a—C13a—N14—C15	19.2 (5)	C26—C27—N28—C28a	57.3 (4)
C13a—N14—C15—C16	5.3 (5)	C27—N28—C28a—C23a	−15.5 (5)
N14—C15—C16—C17	−59.3 (4)	N24—C23a—C28a—N28	4.0 (6)
C15—C16—C17—N18	85.9 (4)	C38a—C33a—N34—C35	15.5 (6)
C16—C17—N18—C18a	−53.4 (4)	C33a—N34—C35—C36	2.7 (5)
C17—N18—C18a—C13a	13.1 (5)	N34—C35—C36—C37	−52.1 (4)
N14—C13a—C18a—N18	−6.3 (6)	C35—C36—C37—N38	83.7 (4)
C28a—C23a—N24—C25	−17.1 (6)	C36—C37—N38—C38a	−58.3 (4)
C23a—N24—C25—C26	−2.6 (5)	C37—N38—C38a—C33a	16.7 (5)
N24—C25—C26—C27	53.9 (4)	N34—C33a—C38a—N38	−3.5 (6)
C25—C26—C27—N28	−84.8 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N18—H18···N32$^{\rm i}$	0.88	2.19	2.976 (4)	149
N28—H28···N12	0.88	2.19	3.000 (5)	153
N38—H38···N22	0.88	2.24	3.022 (4)	148

Symmetry code: (i) $-x, 1-y, 2-z$.

Compound (II)

Crystal data

$C_{19}H_{17}ClN_4$
$M_r = 336.82$
Triclinic, $P\overline{1}$
$a = 9.0066\ (18)$ Å
$b = 17.969\ (4)$ Å
$c = 18.007\ (4)$ Å
$\alpha = 115.73\ (3)°$
$\beta = 101.02\ (3)°$
$\gamma = 98.83\ (3)°$
$V = 2483.1\ (9)$ Å^3
$Z = 6$
$D_x = 1.351$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 212 reflections
$\theta = 3.0$–$27.6°$
$\mu = 0.24$ mm^{-1}
$T = 120\ (1)$ K
Rod, yellow
$0.48 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\rm min} = 0.894$, $T_{\rm max} = 0.977$
37 371 measured reflections
11212 independent reflections
7499 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.108$
$\theta_{\rm max} = 27.6°$
$h = -11 \rightarrow 11$
$k = -23 \rightarrow 23$
$l = -23 \rightarrow 23$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.226$
$S = 1.07$
11 212 reflections
652 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1172P)^2 + 1.3813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.65$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.57$ e Å^{-3}

Compound (I) crystallized in the trigonal system; space group $R\overline{3}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å and an N—H distance of 0.88 Å. The minor component of the disordered seven-membered ring was constrained by use of *DFIX* instructions (*DFIX* 1.52 .005 C5 C61 C61 C71 and *DFIX* 1.46 .005 C71 N8), the C—C and C—N distances being based on those in the major component. The disordered atoms of the minor component were refined isotropically. The site occupancies of the disordered atoms were also refined, with the site-occupancy factors being controlled by a single free variable. Compound (II) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å. The final R factor for (II) of 0.082 is rather large; however, the crystal quality was poor, as is indicated by the value of $R_{\rm int}$, and it proved difficult to obtain better crystals. The largest difference peaks are associated with the Cl atom.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; 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, 2001); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1526). 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.

Chimirri, A., Gitto, R., Grasso, S., Monforte, A. M., Romeo, G. & Zappala, M. (1993). *Heterocycles*, **36**, 865–890.

DeWald, H. A., Lobbestaell, S. & Poschel, B. P. H. (1981). *J. Med. Chem.* **24**, 982–987.

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

Insuasty, B., Insuasty, H., Quiroga, J., Saitz, C. & Jullian, C. (1999). *J. Heterocycl. Chem.* **36**, 635–638.

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

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 & R. M. Sweet, pp. 307–326. London: Academic Press.

Sharp, J. T. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 10, edited by A. R. Katritzky, C. W. Rees & W. Lwowski, p. 593, and references therein. Oxford: Pergamon.

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

Spek, A. L. (2001). *PLATON*. Version of October 2001. University of Utrecht, The Netherlands.

Sternbach, L. H. (1978). *Prog. Drug Res.* **22**, 229–266.