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Four cycloalkanespiro-4′-imidazolidine-2′,5′-dithiones

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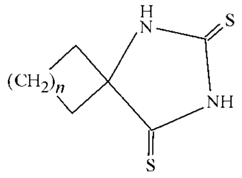
The crystal structures of four cycloalkanespiro-4′-imidazolidine-2′,5′-dithiones, namely cyclopentanespiro-4′-imidazolidine-2′,5′-dithione {systematic name: 1,3-diazaspiro[4.4]nonane-2,4-dithione}, $C_7H_{10}N_2S_2$, cyclohexanespiro-4′-imidazolidine-2′,5′-dithione {systematic name: 1,3-diazaspiro[4.5]decane-2,4-dithione}, $C_8H_{12}N_2S_2$, cycloheptanespiro-4′-imidazolidine-2′,5′-dithione {systematic name: 1,3-diazaspiro[4.6]undecane-2,4-dithione}, $C_9H_{14}N_2S_2$, and cyclooctanespiro-4′-imidazolidine-2′,5′-dithione {systematic name: 1,3-diazaspiro[4.7]dodecane-2,4-dithione}, $C_{10}H_{16}N_2S_2$, have been determined. The three-dimensional packing in all of the structures is based on closely similar chains, in which hydantoin moieties are linked through N—H···S hydrogen bonding. The size of the cycloalkane moiety influences the degree of its deformation. In the cyclooctane compound, the cyclooctane ring assumes both boat–chair and boat–boat conformations.

Comment

The structural characteristics of spirohydantoins are interesting because of their potential biological activities (Somsak *et al.*, 2005). Recently, we began a structural and biological investigation of new hydantoin derivatives and their organometallic complexes (Shivachev *et al.*, 2005). As part of this



(I) $n=2$ (III) $n=4$
(II) $n=3$ (IV) $n=5$

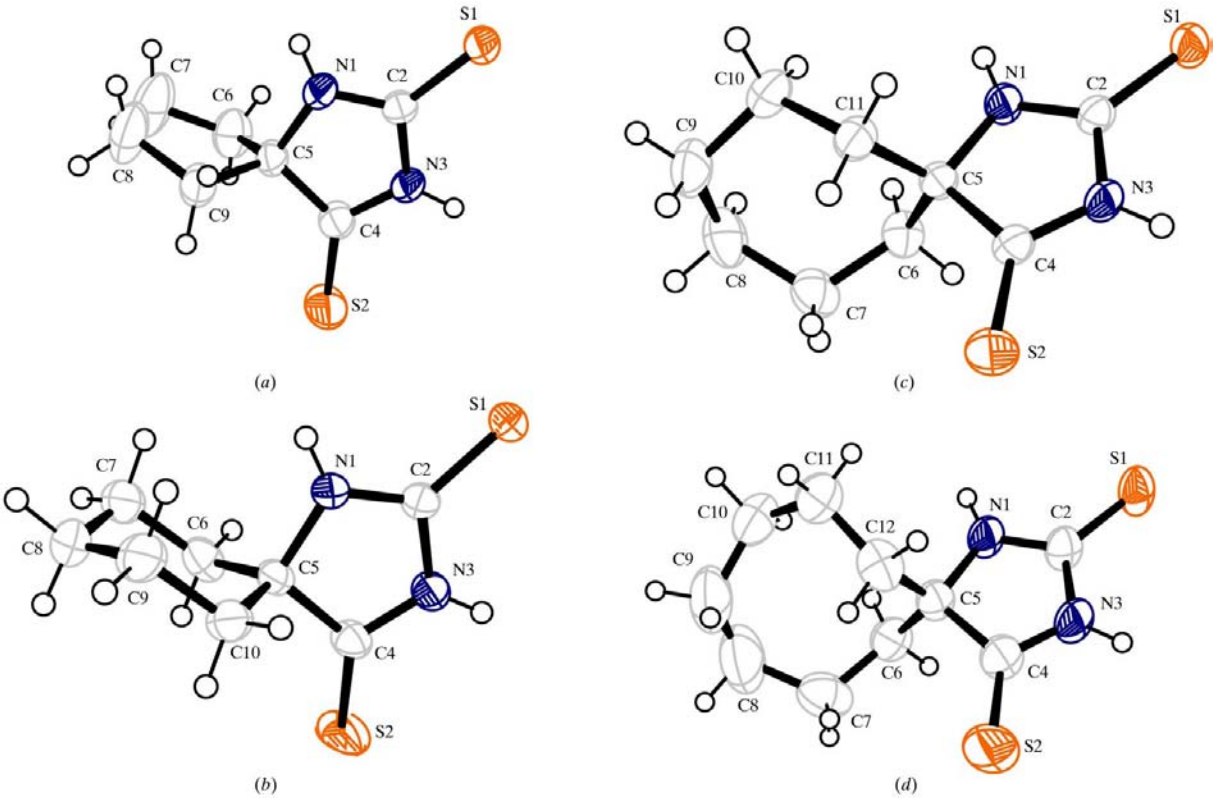


Figure 1
A view of the structure and the atom-numbering scheme of the independent molecule in (*a*) (I), (*b*) (II), (*c*) (III) and (*d*) (IV), showing 50% probability displacement ellipsoids. For compound (IV), only the major (62%) disorder component is represented, the minor (38%) component being omitted for clarity (see *Comment*).

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study, we report for the first time the crystal structures of four cycloalkanespirohydantoindithione derivatives, namely the pentyl, (I), hexyl, (II), heptyl, (III), and octyl, (IV), compounds (Fig. 1). The synthesis and spectroscopic and theoretical *ab initio* calculations for compounds (I)–(IV) have been described elsewhere (Marinov *et al.*, 2005).

For all four structures, only one independent molecule is present in the asymmetric unit. The hydantoin moieties are almost planar, with r.m.s. deviations of 0.017, 0.066, 0.014 and 0.004 Å for the molecules of (I)–(IV), respectively. The bond distances and angles in the hydantoin moieties are comparable to those observed in other spirohydantoins (Gauthier *et al.*, 1997; Shivachev *et al.*, 2005). In (I), the cyclopentane ring adopts an envelope conformation (with C5 as the flap atom), in (II), the cyclohexane ring adopts a chair conformation, while in (III), the cycloheptane ring is in a twist-chair conformation (Allen *et al.*, 1993). The cyclooctane ring in (IV) assumes either a boat–chair (62%) or a boat–boat (38%) conformation (Perez *et al.*, 2005) (see *Experimental*).

The geometric parameters for compounds (I)–(IV) derived from the refined crystal structures (Tables 1, 3, 5 and 7) and *ab initio* calculated gas-phase molecular structures correspond in general. The bond distances calculated at the HF/3–21G* level in the theoretical models are slightly longer than those obtained from crystal structure determination. The largest discrepancy is for the C2—N1 bond, where the average discrepancy is 0.02 Å. The only exception is the C2═S1 bond length, which is slightly shorter in all theoretical models; we attribute this shortening to the absence of hydrogen bonding in the theoretical models. Experimental confirmation of the difference between the C2═S1 and C4═S2 bonds observed in the computational model shows that the elongation of the C═S bond at the 2′-position is a fundamental feature of the spirohydantoin molecular structure. Another tendency suggested by the theoretical model is a relationship between the C5—C4 bond length [1.526, 1.535, 1.539 and 1.542 Å for (I)–(IV), respectively] and the size of the cycloalkane derivative. The values of the corresponding experimental bond lengths are 1.519 (4), 1.520 (2), 1.530 (2) and 1.525 (4) Å. Taking into account the standard uncertainties, the apparent differences between the experimental bond lengths were shown to be insignificant.

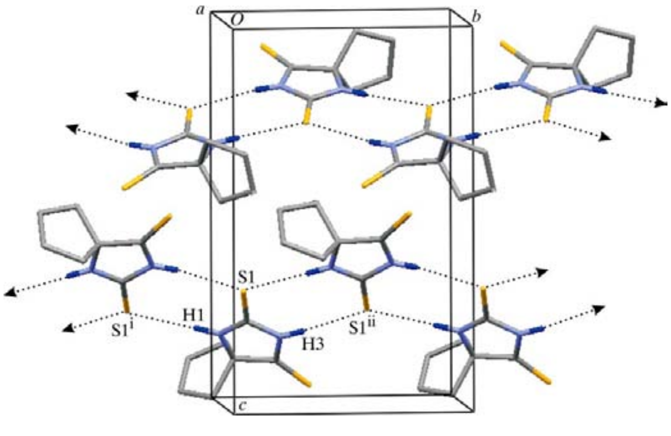

Figure 2
A partial view of the molecular packing in (I). Dotted lines represent N—H···S hydrogen bonds. [Symmetry codes: (i) $-x$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$; (ii) $-x$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$.]

The molecular packing in (I)–(IV) is mainly governed by two factors, namely, the hydrogen-bonding properties of the hydantoin moiety and the size of the cycloalkane ring. In all structures, the organic molecules are arranged in chains in which hydantoin moieties are linked through N—H···S hydrogen-bonded rings involving atom S1 (Tables 2, 4, 6 and 8). In compounds (I) and (IV), these rings are generated by a screw axis and have one H1 atom and one H3 atom in each ring. Thus, the chains for these compounds can be described

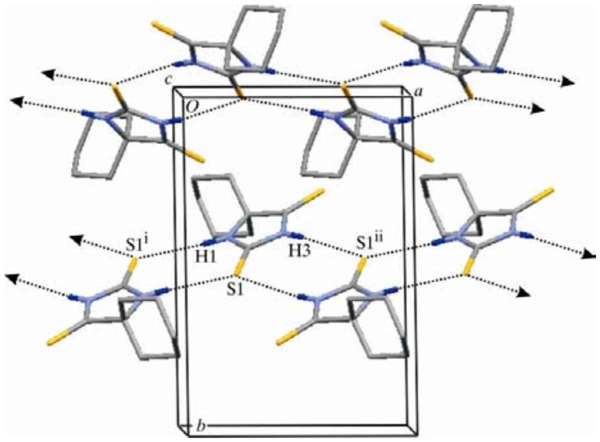

Figure 3
A partial view of the molecular packing in (II). Dotted lines represent N—H···S hydrogen bonds. [Symmetry codes: (i) $-x$, $-y + 1$, $-z$; (ii) $-x + 1$, $-y + 1$, $-z$.]

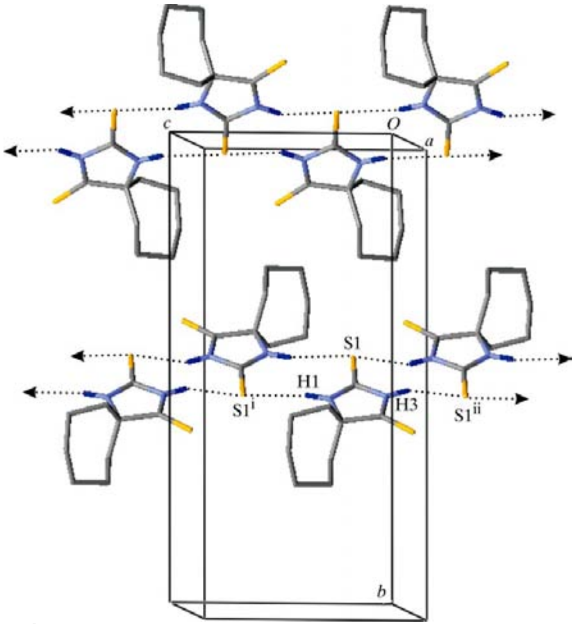

Figure 4
A partial view of the molecular packing in (III). Hydrogen bonds are indicated by dotted lines. [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x + 1$, $-y + 1$, $-z$.]

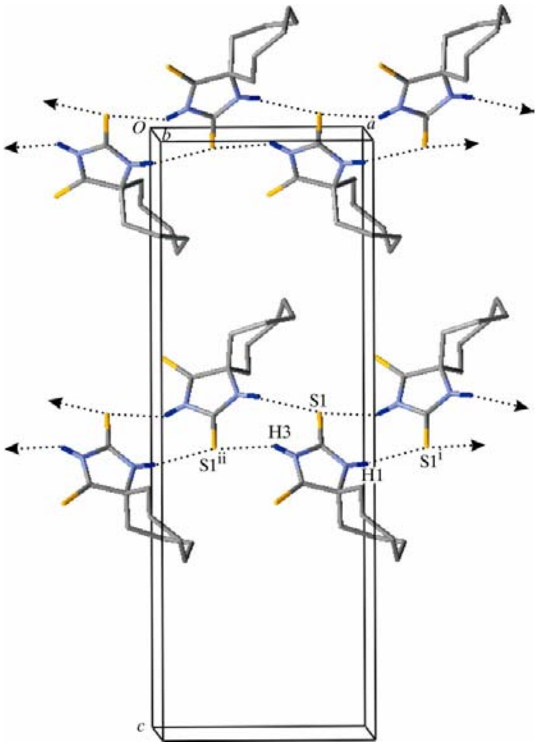

Figure 5
A partial view of the molecular packing in (IV). Hydrogen bonds are indicated by dotted lines. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]

by the graph-set notation $C(4)[R_2^2(8)]$ (Etter *et al.*, 1990). A search of the Cambridge Structural Database (Allen, 2002) performed by Yu *et al.* (2004) showed that six of the hydantoin structures are built up of similar chains, where one O atom analogous to atom S1 accepts two hydrogen bonds. In contrast, the extended structures of (II) and (III) comprise $C(6)[R_2^2(8)]$ chains, where the $R_2^2(8)$ rings are generated by inversion and have two H1 atoms and two H3 atoms in successive rings. It is interesting to note that the same chains of rings involving atom S1 are formed in two different ways. It appears that this arrangement is common for this type of molecule, and further investigations will determine if the reason is steric (because S1 is more accessible than S2, which lies adjacent to a cycloalkyl ring); another factor could be different charges on S1 and S2. The similarity of the chain structures imparts almost the same values to the cell directions along which the chains propagate [the *b* axis in (I), the *a* axis in (II) and (IV), and the *c* axis in (III)] (Figs. 2–5). While the hydantoin moiety is responsible for the chain-like arrangement of the organic molecules, the cycloalkane moiety determines the three-dimensional arrangement of these chains.

Experimental

Compounds (I)–(IV) were prepared according to the method described by Marinov *et al.* (2005). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a methanol solution at 277 K.

Compound (I)

Crystal data

$C_7H_{10}N_2S_2$
$M_r = 186.29$
Orthorhombic, $P2_12_12_1$
$a = 7.898$ (5) Å
$b = 8.4607$ (19) Å
$c = 13.587$ (2) Å
$V = 907.9$ (6) Å^3
$Z = 4$
$D_x = 1.363$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 20.3$–$20.7°$
$\mu = 0.52$ mm^{-1}
$T = 290$ (2) K
Square prism, orange
0.24 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2483 measured reflections
2198 independent reflections
1629 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$

$\theta_{\rm max} = 28.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.126$
$S = 1.05$
2198 reflections
100 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.3808P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 911 Friedel pairs
Flack parameter: 0.06 (16)

Table 1
Selected bond lengths (Å) for (I).

C2—N1	1.309 (4)	C4—C5	1.519 (4)
C2—N3	1.366 (4)	C4—S2	1.622 (4)
C2—S1	1.674 (3)	C5—N1	1.463 (4)
C4—N3	1.353 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.86	2.51	3.375 (3)	179
N3—H3···S1^{ii}	0.86	2.49	3.332 (3)	167

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

Compound (II)

Crystal data

$C_8H_{12}N_2S_2$
$M_r = 200.32$
Monoclinic, $P2_1/n$
$a = 8.6896$ (10) Å
$b = 12.2674$ (15) Å
$c = 9.7864$ (10) Å
$\beta = 109.86$ (9)°
$V = 981.2$ (6) Å^3
$Z = 4$

$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 20.5$–$21.5°$
$\mu = 0.49$ mm^{-1}
$T = 290$ (2) K
Cube, yellow
0.45 × 0.45 × 0.45 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4892 measured reflections
2356 independent reflections
2036 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

$\theta_{\rm max} = 28.0°$
$h = 0 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 0.99$
2356 reflections
110 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.2697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.097 (6)

Table 3
Selected bond lengths (Å) for (II).

S1—C2	1.6669 (16)	N1—C2	1.318 (2)
S2—C4	1.627 (2)	N1—C5	1.473 (2)
N3—C4	1.3524 (19)	C4—C5	1.520 (2)
N3—C2	1.380 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.86	2.61	3.4665 (17)	178
N3—H3···S1^{ii}	0.86	2.58	3.3959 (16)	160

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

Compound (III)

Crystal data

$C_9H_{14}N_2S_2$
$M_r = 214.34$
Monoclinic, $P2_1/n$
$a = 7.4041$ (14) Å
$b = 17.859$ (4) Å
$c = 8.4491$ (14) Å
$\beta = 105.848$ (19)°
$V = 1074.7$ (4) Å^3
$Z = 4$
$D_x = 1.325$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 18.4$–19.8°
$\mu = 0.45$ mm^{-1}
$T = 290$ (2) K
Cube, yellow
0.33 × 0.33 × 0.33 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
5464 measured reflections
2591 independent reflections
2042 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

$\theta_{max} = 28.0°$
$h = 0 \rightarrow 9$
$k = -23 \rightarrow 23$
$l = -11 \rightarrow 10$
3 standard reflections
every 500 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.091$
$S = 1.00$
2591 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.254P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 5
Selected bond lengths (Å) for (III).

S1—C2	1.6676 (16)	N3—C4	1.349 (2)
S2—C4	1.6263 (16)	N3—C2	1.3795 (19)
N1—C2	1.3169 (19)	C4—C5	1.530 (2)
N1—C5	1.4717 (19)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.86	2.51	3.3618 (14)	172
N3—H3···S1^{ii}	0.86	2.52	3.3460 (15)	161

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

Compound (IV)

Crystal data

$C_{10}H_{16}N_2S_2$
$M_r = 228.37$
Orthorhombic, $Pbca$
$a = 8.484$ (2) Å
$b = 11.5018$ (18) Å
$c = 23.992$ (10) Å
$V = 2341.2$ (12) Å^3
$Z = 8$
$D_x = 1.296$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 17.9$–19.1°
$\mu = 0.42$ mm^{-1}
$T = 290$ (2) K
Square prism, yellow
0.40 × 0.38 × 0.36 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
10820 measured reflections
2812 independent reflections
1730 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

$\theta_{max} = 28.0°$
$h = 0 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -31 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.174$
$S = 1.02$
2812 reflections
136 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 1.361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 7
Selected bond lengths (Å) for (IV).

N1—C2	1.317 (3)	S1—C2	1.664 (3)
N1—C5	1.467 (4)	S2—C4	1.627 (3)
N3—C4	1.350 (4)	C4—C5	1.525 (4)
N3—C2	1.376 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.86	2.56	3.376 (2)	159
N3—H3···S1^{ii}	0.86	2.62	3.367 (3)	146

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

H atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.86 Å) and constrained to ride on their parent atoms, with U_{iso}(H) values of $1.2U_{eq}$(C,N). Disorder of atom C10 in the cyclooctane ring in (IV) was modelled by competitive refinement of two alternative sites. The major [0.622 (8)] and minor [0.378 (2)] occupancies correspond to boat–chair and boat–boat conformations, respectively.

For all four compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to

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refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1624). Services for accessing these data are described at the back of the journal.

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