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The Conformation of Heterocyclic Spiro Compounds.
II. The Crystal and Molecular Structure of *N*-Methylgranatanine-3-spiro-5′-hydantoin

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Crystals of *N*-methylgranatanine-3-spiro-5′-hydantoin, $C_{11}H_{17}N_3O_2$, are monoclinic, space group $P2_1$, with a = 13·889 (2), b = 11·913 (1), c = 6·971 (1) Å, β = 93·56 (1)°, and four molecules in the unit cell. The structure was determined by direct methods and refined by Fourier and least-squares calculations. The bicyclo[3.3.1]nonane system of the molecule adopts a flattened double-chair conformation.

Introduction

As part of an investigation of the pharmacological properties of the heterocyclic spiro derivatives of nortropane and granatanine systems (Gonzalez Trigo, Avendaño & Martínez Moreno, 1974), the structure of *N*-methyltropane-3-spiro-5′-hydantoin was recently determined (Smith-Verdier, Florencio & García-Blanco, 1977). In the present paper the crystal structure of *N*-methylgranatanine-3-spiro-5′-hydantoin is reported. This compound belongs to the bicyclo[3.3.1]nonane system and, in view of the divergence of opinion over the preferred conformation, it is of interest to determine the conformation of its molecule. On the one hand, NMR studies of 3-α-granatanol by Chen & Lefevre (1966) seemingly indicated an equilibrium between boat and chair conformations for the piperidinol ring, on the other hand, IR studies by Aaron, Ferguson & Rader (1967) pointed to the presence of a fixed distorted double-chair conformation in the same system.

Recently, the structures of several bicyclo[3.3.1]nonane derivatives have been reported: 1-*p*-bromobenzenesulphonyloxymethyl-5-methylbicyclo[3.3.1]nonan-9-ol (Brown, Martin & Sim, 1965), 2-chlorobicyclo[3.3.1]nonan-9-one (Webb & Becker, 1967), 1,7-dimethoxycarbonyl-3a,7-methano-3a*H*-decahydrocyclopentacyclooctene-2,10-dione (Abola, Pletcher & Sax, 1974), 9-benzoyl-3α-bromo-2β-hydroxy-9-azabicyclo[3.3.1]nonane (Tamura & Sim, 1968) and 1,2,4,4,5,8-hexamethyl-8-*N*-acetamidobicyclo[3.3.1]-3-azanon-2-ene (García-Blanco, Florencio & Smith-Verdier, 1976). These studies have shown that the bicyclo[3.3.1]nonane system assumes a twin-chair conformation in all compounds except 1,7-methoxycarbonyl-3a,7-methano-3a*H*-decahydrocyclopentacyclooctene-2,10-dione in which it has a partial boat-chair conformation and 9-benzoyl-3α-bromo-2β-hydroxy-9-azabicyclo[3.3.1]nonane in which it adopts a boat-chair conformation. In the present compound, Gonzalez Trigo *et al.* (1974) found from NMR studies that the boat-chair is the preferred conformation, but our data showed that in the solid state a distorted double-chair conformation is favoured.

Experimental

Samples of *N*-methylgranatanine-3-spiro-5′-hydantoin were obtained through the courtesy of Drs C. Avendaño and M. Martínez Moreno of the Departamento de Química Orgánica y Farmaceutica de la Facultad de Farmacia de la Universidad Complutense de Madrid. The unit-cell parameters and the intensity data were measured on a Philips PW 1100 automatic diffractometer monochromated with a graphite crystal. The crystal data are summarized in Table 1. A θ–2θ scanning mode with Mo $K\alpha$ radiation was used to measure 3503 independent reflections with 2θ values below 30°; 3281 of these were considered as observed [a reflection was considered as observed if its intensity was greater than $2{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics]. The intensity data were reduced to structure factors, and no absorption correction was applied ($\mu = 0{\cdot}9645$ cm^{-1}).

Table 1. *Crystal data*

Chemical formula: $C_{11}H_{17}N_3O_2$
Crystal system: monoclinic
Space group: $P2_1$
a = 13·889 (2) Å*
b = 11·913 (1)
c = 6·971 (1)
β = 93·56 (1)°
V = 1151·16 Å^3
Z = 4
$F(000)$ = 480
D_x = 1·279 g cm^{-3}
D_m = 1·27 (flotation in KI)
λ(Mo $K\alpha$) = 0·7107 Å
Crystal dimensions: 0·38 × 0·42 × 0·40 mm

* Cell dimensions were obtained from + and − 2θ values of 36 reflections.

Structure determination and refinement

There are two crystallographically independent molecules in one asymmetric unit of the crystal. The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An E map generated from the phase set (150 reflections) with the highest combined figure of merit located a small fragment of one of the two independent molecules (8 atoms), the remaining atoms of this molecule and part of the other (11 atoms) were found by means of one cycle of tangent refinement. The remaining non-hydrogen atoms were located from a Fourier synthesis. Isotropic refinement of the non-hydrogen atoms gave $R = 0{\cdot}148$. Further refinement with anisotropic temperature factors reduced R to 0·083. The H atoms were then found from a difference synthesis and included with isotropic temperature factors (the value of the adjacent heavy atom). The refinement continued to a stage at which no parameter shift was significant. The final R value was 0·046 and the weighted value R_w was 0·060 $\{$where $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$. One analysis of the distribution of $\langle w\Delta^2\rangle$ with both $\sin\theta$ and $\langle F\rangle$ confirmed that the weighting scheme used was reasonable. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).

Table 2. *Positional parameters* ($\times 10^4$) *for the heavy atoms*

	x	*y*	*z*
C(1*A*)	4449 (1)	1581 (0)	4088 (2)
C(2*A*)	3541 (1)	1701 (2)	5240 (3)
C(3,5'*A*)	2608 (1)	1182 (1)	4320 (2)
C(4*A*)	2575 (1)	1205 (2)	2092 (2)
C(5*A*)	3541 (1)	1207 (2)	1118 (2)
N(6*A*)	4257 (1)	1954 (1)	2079 (2)
C(7*A*)	4894 (1)	409 (2)	4074 (3)
C(8*A*)	4340 (1)	−445 (2)	2803 (4)
C(9*A*)	4001 (1)	62 (2)	892 (3)
C(10*A*)	4015 (2)	3142 (2)	1896 (5)
N(1'*A*)	2382 (1)	86 (1)	5126 (3)
C(2'*A*)	1553 (1)	104 (2)	6057 (3)
N(3'*A*)	1141 (1)	1159 (1)	5822 (3)
C(4'*A*)	1729 (1)	1867 (2)	4896 (3)
O(1*A*)	1205 (1)	−650 (1)	6964 (3)
O(2*A*)	1588 (1)	2850 (1)	4561 (4)
C(1*B*)	8926 (1)	2516 (1)	7198 (3)
C(2*B*)	7881 (1)	2570 (1)	7791 (3)
C(3,5'*B*)	7640 (1)	1863 (1)	9540 (2)
C(4*B*)	8229 (1)	758 (1)	9661 (2)
C(5*B*)	9249 (1)	793 (1)	8925 (3)
N(6*B*)	9263 (1)	1349 (1)	7036 (2)
C(7*B*)	9673 (1)	3148 (2)	8504 (5)
C(8*B*)	9946 (1)	2583 (3)	10414 (4)
C(9*B*)	10030 (1)	1311 (2)	10243 (3)
C(10*B*)	8755 (2)	711 (2)	5484 (3)
N(1'*B*)	7662 (1)	2504 (1)	11342 (2)
C(2'*B*)	6770 (1)	2630 (1)	12008 (2)
N(3'*B*)	6126 (1)	2018 (1)	10828 (2)
C(4'*B*)	6559 (1)	1544 (2)	9340 (3)
O(1*B*)	6550 (1)	3167 (1)	13408 (2)
O(2*B*)	6181 (1)	963 (2)	8088 (3)

Table 3. *Atomic positional* ($\times 10^3$) *and thermal* ($\times 10^4$) *parameters for the* H *atoms*

	x	*y*	*z*	*U* (Å^2)
H(1*A*)	495 (3)	205 (3)	476 (5)	28 (8)
H(21*A*)	366 (2)	137 (3)	657 (5)	29 (8)
H(22*A*)	344 (3)	245 (4)	553 (6)	44 (11)
H(3'*A*)	54 (2)	131 (3)	619 (5)	32 (9)
H(41*A*)	218 (3)	64 (3)	168 (6)	36 (10)
H(42*A*)	222 (2)	187 (3)	175 (4)	20 (7)
H(5*A*)	341 (2)	153 (2)	−008 (4)	13 (6)
H(71*A*)	556 (3)	41 (4)	369 (6)	46 (12)
H(72*A*)	501 (3)	517 (3)	473 (5)	30 (9)
H(81*A*)	379 (2)	−74 (3)	340 (4)	19 (7)
H(82*A*)	470 (2)	−108 (3)	262 (5)	33 (9)
H(91*A*)	355 (2)	−45 (3)	017 (5)	24 (7)
H(92*A*)	455 (2)	17 (3)	012 (5)	28 (8)
H(101*A*)	392 (3)	330 (4)	067 (7)	51 (12)
H(102*A*)	445 (3)	361 (3)	207 (6)	37 (10)
H(103*A*)	340 (3)	333 (3)	233 (5)	33 (9)
H(1'*A*)	276 (2)	−47 (3)	547 (4)	18 (6)
H(1*B*)	892 (2)	279 (2)	589 (4)	14 (6)
H(21*B*)	748 (2)	234 (2)	678 (4)	12 (6)
H(22*B*)	772 (2)	335 (3)	813 (6)	35 (9)
H(41*B*)	787 (2)	24 (2)	883 (4)	11 (6)
H(42*B*)	828 (2)	44 (3)	094 (5)	29 (8)
H(5*B*)	943 (2)	2 (3)	866 (4)	19 (7)
H(71*B*)	941 (3)	384 (3)	869 (6)	35 (9)
H(72*B*)	1023 (3)	319 (4)	764 (6)	44 (11)
H(81*B*)	945 (2)	278 (3)	1142 (5)	27 (8)
H(82*B*)	1058 (3)	289 (4)	1089 (6)	45 (11)
H(91*B*)	1004 (3)	92 (4)	1145 (6)	47 (12)
H(92*B*)	1068 (2)	112 (3)	977 (5)	24 (7)
H(101*B*)	886 (3)	118 (4)	442 (6)	39 (10)
H(102*B*)	806 (3)	61 (4)	568 (7)	50 (12)
H(103*B*)	905 (3)	−4 (4)	534 (5)	36 (10)
H(1'*B*)	816 (2)	301 (3)	1175 (5)	24 (7)
H(3'*B*)	557 (2)	193 (3)	1108 (5)	26 (8)

Computations were carried out with programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) running on the Univac 1108 computer of the Centro de Procesos de Datos del Ministerio de Educación y Ciencia (Madrid).

The final positional parameters of the non-hydrogen atoms are given in Table 2, and those of the H atoms in Table 3.*

Discussion

Fig. 1 shows the two independent molecules in the asymmetric unit. There are no significant structural

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33220 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

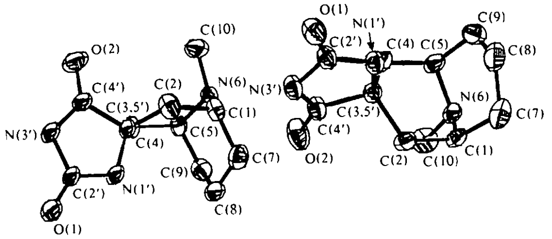

Fig. 1. *ORTEP* drawing of the two independent molecules. Thermal ellipsoids are drawn at 50% probability.

Table 4. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
N(1')–C(2')	1·357 (6)	1·357 (5)
N(3')–C(2')	1·388 (3)	1·386 (6)
N(3')–C(4')	1·366 (5)	1·355 (5)
O(1)–C(2')	1·217 (4)	1·222 (4)
O(2)–C(4')	1·209 (3)	1·208 (5)
C(1)–C(2)	1·542 (7)	1·534 (5)
C(1)–N(6)	1·478 (4)	1·476 (3)
C(1)–C(7)	1·530 (3)	1·535 (7)
C(2)–C(3,5')	1·541 (6)	1·537 (4)
C(3,5')–C(4)	1·552 (3)	1·551 (3)
C(3,5')–N(1')	1·464 (3)	1·469 (3)
C(3,5')–C(4')	1·542 (4)	1·547 (3)
C(4)–C(5)	1·541 (6)	1·537 (6)
C(5)–N(6)	1·466 (5)	1·475 (3)
C(5)–C(9)	1·521 (4)	1·510 (7)
N(6)–C(10)	1·460 (3)	1·467 (6)
C(7)–C(8)	1·527 (6)	1·519 (6)
C(8)–C(9)	1·511 (6)	1·527 (5)

	Molecule *A*	Molecule *B*
C(3,5')–N(1')–C(2')	112·2 (2)	112·3 (3)
N(1')–C(2')–N(3')	108·3 (2)	108·0 (2)
N(1')–C(2')–O(1)	127·8 (2)	127·6 (2)
O(1)–C(2')–N(3')	123·9 (2)	124·5 (2)
C(2')–N(3')–C(4')	111·2 (2)	111·9 (2)
N(3')–C(4')–C(3,5')	107·5 (2)	107·6 (2)
N(3')–C(4')–O(2)	126·7 (3)	126·8 (2)
O(2)–C(4')–C(3,5')	125·8 (3)	125·6 (2)
C(2)–C(1)–N(6)	111·1 (2)	111·7 (2)
C(7)–C(1)–N(6)	108·6 (2)	107·6 (2)
C(7)–C(1)–C(2)	115·6 (2)	115·8 (2)
C(1)–C(2)–C(3,5')	116·1 (2)	116·5 (2)
C(2)–C(3,5')–C(4)	112·4 (2)	111·7 (2)
C(2)–C(3,5')–C(4')	109·7 (2)	108·8 (2)
N(1')–C(3,5')–C(4')	100·5 (2)	100·0 (2)
N(1')–C(3,5')–C(4)	114·0 (2)	114·4 (2)
C(5)–C(4)–C(3,5')	118·0 (2)	117·0 (2)
N(6)–C(5)–C(4)	112·6 (2)	111·9 (2)
N(6)–C(5)–C(9)	108·4 (2)	108·1 (2)
C(4)–C(5)–C(9)	115·3 (2)	116·7 (2)
C(1)–N(6)–C(5)	109·1 (2)	109·5 (2)
C(5)–N(6)–C(10)	113·9 (2)	113·1 (2)
C(1)–N(6)–C(10)	113·7 (2)	113·9 (2)
C(1)–C(7)–C(8)	115·1 (2)	115·1 (2)
C(7)–C(8)–C(9)	111·3 (2)	112·9 (2)
C(5)–C(9)–C(8)	112·2 (2)	113·5 (2)

Table 5. *Some least-squares planes and distances* (Å) *of atoms from these planes*

Atoms used in fitting the least-squares planes are denoted by asterisks.

Plane 1(*A*): $0{\cdot}4959X + 0{\cdot}1719Y + 0{\cdot}8512Z = 4{\cdot}5030$
Plane 1(*B*): $-0{\cdot}1387X + 0{\cdot}8561Y - 0{\cdot}4978Z = -2{\cdot}8172$

	Molecule *A*	Molecule *B*
C(3,5')*	0·001	0·001
C(10)*	−0·011	−0·010
N(6)*	0·016	0·015
C(8)*	−0·006	−0·006
C(1)	1·219	1·217
C(2)	1·276	1·272
C(4)	−1·289	−1·282
C(5)	−1·179	−1·193
C(7)	1·277	1·274
C(9)	−1·226	−1·263
N(1')	0·081	0·039
C(4')	−0·135	−0·049
O(2)	−0·221	−0·143
C(2')	0·046	0·111
N(3')	−0·153	0·012
O(1)	0·168	0·222

Plane 2(*A*): $-0{\cdot}0617X + 0{\cdot}9768Y - 0{\cdot}2053Z = 0{\cdot}9173$
Plane 2(*B*): $0{\cdot}2598X + 0{\cdot}5278Y - 0{\cdot}8086Z = 8{\cdot}7667$

C(1)*	−0·029	0·009
C(2)*	0·027	−0·008
C(4)*	−0·027	0·008
C(5)*	0·029	−0·009
C(3,5')	−0·369	0·424
N(6)	0·703	−0·694

Plane 3(*A*): $0{\cdot}7830X + 0{\cdot}3883Y - 0{\cdot}4860Z = 4{\cdot}0218$
Plane 3(*B*): $0{\cdot}7352X - 0{\cdot}2251Y - 0{\cdot}6394Z = 4{\cdot}9931$

C(1)*	0·028	0·015
C(5)*	−0·028	−0·015
C(7)*	−0·026	−0·014
C(9)*	0·027	0·014
C(8)	−0·552	−0·495
N(6)	0·739	0·750

Plane 4(*A*): $0{\cdot}7541X - 0{\cdot}5916Y - 0{\cdot}2853Z = 2{\cdot}5981$
Plane 4(*B*): $0{\cdot}9283X + 0{\cdot}2985Y + 0{\cdot}2219Z = 13{\cdot}2259$

C(1)*	0·000	0·000
N(6)*	0·000	0·000
C(5)*	0·000	0·000
C(3,5')	−1·700	−1·623
C(8)	1·613	1·706
C(2)	−1·301	−1·260
C(4)	−1·235	−1·243
C(7)	1·297	1·337
C(9)	1·343	1·343

Plane 5(*A*): $0{\cdot}4367X + 0{\cdot}2643Y + 0{\cdot}8599Z = 4{\cdot}4577$
Plane 5(*B*): $-0{\cdot}1429X + 0{\cdot}8254Y - 0{\cdot}5462Z = -3{\cdot}2676$

N(1')*	−0·016	−0·027
C(2')*	0·027	0·024
N(3')*	−0·027	−0·009
C(4')*	0·016	−0·006
C(3,5')*	−0·000	0·019
O(1)	0·103	0·074
O(2)	0·047	−0·035

differences between them. Table 4 lists the bond lengths and angles. The displacements of some atoms from several least-squares planes are given in Table 5.

The average standard deviations in bond distances and bond angles are 0·005 Å and 0·2° respectively. The dimensions in the two independent molecules agree within three standard deviations. In Fig. 2 the average bond distances and bond angles are shown.

The molecule contains two six-membered rings, (I) and (II), joined by a common C—N—C bridge with a CH_3 group attached to the N atom and a hydantoin ring substituted at the spiranic C(3,5′) (Fig. 1).

The molecular symmetry approximates to *m* [a mirror plane defined by C(3,5′), N(6), C(8) and C(10) (plane 1, Table 5)]. The atoms belonging to the hydantoin ring are approximately in this plane, O(1) and O(2) showing the greatest displacement. The two cyclohexane rings have chair conformations. In ring (I) (molecule *A*), the displacements of C(3,5′) and N(6) from the plane through the remaining atoms (plane 2) are —0·361 and 0·703 Å respectively; the corresponding displacements in molecule *B* are 0·424 and —0·694 Å. In ring (II) (plane 3) there is an identical pattern: in molecule *A*, the displacements of C(8) and N(6) from the plane through C(1), C(5), C(7) and C(9) are —0·552 and 0·739 Å; in molecule *B* these displacements are —0·495 and 0·750 Å respectively. These values show that N(6) belonging to the two rings is displaced with respect to the two rings closer to the value calculated for the ideal chair (Brown, Martin & Sim, 1965) than those values found for the displacements of C(3,5′) and C(8); consequently, the C(1), C(2), C(3,5′), C(4), C(5), and C(1), C(5), C(7), C(8), C(9) parts of rings (I) and (II) are more flattened.

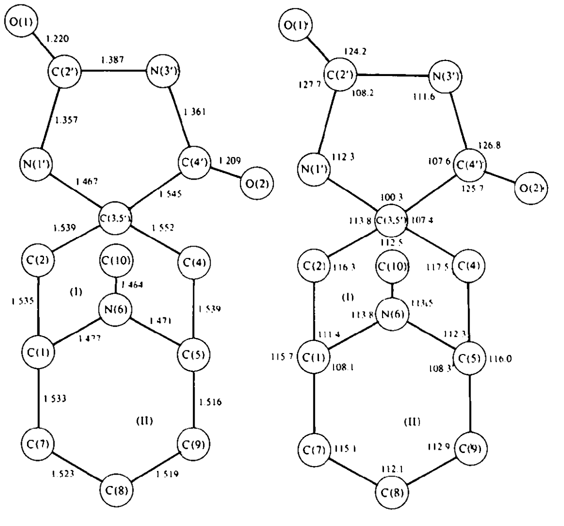

Fig. 2. The average bond lengths (Å) and angles (°) involving the non-hydrogen atoms. Angles not shown: C(2)—C(3,5′)—C(4′) = 109·3°, and C(4)—C(3,5′)—N(1′) = 114·2°.

The flattening of the cyclohexane rings is also clearly shown in the displacements of the atoms from the plane through C(1), N(6) and C(5) (plane 4); in the ideal twin-chair conformation, the displacements of C(3,5′) and C(8) would not differ from the displacements of C(2), C(4), C(7) and C(9), whereas, in fact, the average displacements of C(3,5′) and C(8) (1·656 Å in molecule *A*, and 1·665 Å in molecule *B*) are considerably larger than the average displacements of C(2), C(4), C(7) and C(9) (1·294 Å in molecule *A*, and 1·296 Å in molecule *B*). This flattening is due to the strong steric interaction between the C(8) methylene group and the hydantoin group attached to C(3,5′). This interaction is clearly reflected in the large value of the C(3,5′)···C(8) non-bonded separation (3·315 Å in molecule *A*, and 3·334 Å in molecule *B*).

The CH_3 group is in an axial position with respect to ring (I) in both molecules *A* and *B*.

The average values for angles at the C atoms involved in the flattening of the rings, *i.e.* C(2), C(3,5′), C(4), C(7), C(8) and C(9) (Fig. 2), are necessarily larger than tetrahedral. The values of the angles C(2)—C(1)—C(7) and C(4)—C(5)—C(9) (both 116°) are significantly larger than those reported for similar bond angles by Brown, Martin & Sim (1965) (112 and 113°) and Tamura & Sim (1968) (113°).

The asymmetry parameters (Duax & Norton, 1975)

Table 6. *Asymmetry parameters*

	(1)	(2)	(3)
Molecule *A*			
Ring (I)	$\Delta C_s^{3,5'} = 6{\cdot}07$	$\Delta C_2^{1-6} = 10{\cdot}47$	$\Delta C_2^{1-2} = 32{\cdot}73$
Ring (II)	$\Delta C_2^{5-6} = 4{\cdot}34$	$\Delta C_s^{6} = 6{\cdot}08$	$\Delta C_s^{1} = 18{\cdot}17$
Molecule *B*			
Ring (I)	$\Delta C_s^{3,5'} = 1{\cdot}96$	$\Delta C_2^{1-6} = 12{\cdot}05$	$\Delta C_2^{1-2} = 28{\cdot}16$
Ring (II)	$\Delta C_s^{6} = 3{\cdot}25$	$\Delta C_2^{5-6} = 10{\cdot}39$	$\Delta C_2^{1-7} = 27{\cdot}25$

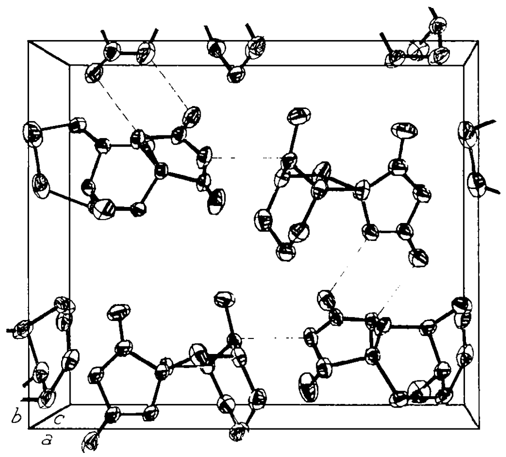

Fig. 3. Packing diagram. The broken lines are hydrogen bonds.

(Table 6) show that mirror symmetry is dominant in ring (I) of molecules *A* and *B*, with an approximate C_s plane passing through C(3,5′) and N(6). In ring (II) of molecule *A*, the rotational symmetry is dominant [an approximate C_2 axis intersects the C(5)–C(6) and C(7)–C(8) bonds], whereas in ring (II) of molecule *B*, according to the asymmetry parameter, mirror symmetry is dominant with an approximate C_s plane passing through N(6) and C(8).

The hydantoin ring is practically planar. Bond lengths and bond angles (Fig. 2) are in good agreement with those found in *N*-methyltropane-3-spiro-5′-hydantoin (Smith-Verdier, Florencio & García-Blanco, 1977).

Bond lengths and bond angles involving H atoms are given in Table 7.

Fig. 3 shows the packing of the molecules in the crystal.

There are three crystallographically independent hydrogen bonds in the crystal structure: N(3′*B*)–H···N(6*A*), N(1′*A*)($\bar{x}$, $\frac{1}{2}+y$, $\bar{z}$)–H···O(1*B*) and N(1′*B*)–H···O(1*A*)($\bar{x}$, $\frac{1}{2}+y$, $\bar{z}$). The geometries of these H bonds are given in Table 8. Other molecular distances correspond to van der Waals interactions.

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Table 7. *Bond lengths* (Å) *and angles* (°) *involving H atoms*

	Molecule *A*	Molecule *B*
C(1)–H(1)	0·99 (4)	0·97 (3)
C(2)–H(2,1)	1·01 (4)	0·92 (3)
C(2)–H(2,2)	0·93 (5)	0·99 (5)
C(4)–H(4,1)	0·91 (5)	0·96 (3)
C(4)–H(4,2)	0·96 (4)	0·97 (4)
C(5)–H(5)	0·93 (3)	0·98 (4)
C(7)–H(7,1)	0·98 (5)	0·91 (5)
C(7)–H(7,2)	0·88 (4)	1·01 (5)
C(8)–H(8,1)	0·96 (4)	1·03 (4)
C(8)–H(8,2)	0·92 (5)	0·99 (5)
C(9)–H(9,1)	0·99 (4)	0·96 (5)
C(9)–H(9,2)	0·97 (4)	1·01 (4)
C(10)–H(10,1)	0·89 (5)	0·95 (5)
C(10)–H(10,2)	0·83 (5)	0·99 (5)
C(10)–H(10,3)	0·95 (4)	0·99 (5)

	Molecule *A*	Molecule *B*
C(2)–C(1)–H(1)	106 (2)	106 (2)
C(7)–C(1)–H(1)	104 (2)	111 (2)
N(6)–C(1)–H(1)	111 (2)	104 (2)
C(3,5′)–C(2)–H(2,1)	108 (2)	107 (2)
C(3,5′)–C(2)–H(2,2)	110 (3)	105 (3)
C(1)–C(2)–H(2,2)	110 (3)	109 (2)
C(1)–C(2)–H(2,1)	110 (2)	109 (2)
H(2,1)–C(2)–H(2,2)	101 (4)	109 (3)
C(3,5′)–C(4)–H(4,1)	106 (3)	105 (2)
C(3,5′)–C(4)–H(4,2)	104 (2)	113 (3)
C(5)–C(4)–H(4,2)	110 (2)	107 (2)
C(5)–C(4)–H(4,1)	113 (3)	106 (2)
H(4,1)–C(4)–H(4,2)	105 (4)	108 (3)
C(4)–C(5)–H(5)	105 (2)	107 (2)
C(9)–C(5)–H(5)	110 (2)	108 (2)
N(6)–C(5)–H(5)	104 (2)	104 (2)
C(1)–C(7)–H(7,1)	113 (3)	106 (3)
C(8)–C(7)–H(7,1)	107 (3)	111 (3)
C(1)–C(7)–H(7,2)	109 (3)	101 (3)
C(8)–C(7)–H(7,2)	112 (3)	112 (3)
H(7,1)–C(7)–H(7,2)	100 (4)	112 (4)
C(7)–C(8)–H(8,1)	112 (2)	111 (2)
C(7)–C(8)–H(8,2)	112 (3)	107 (3)
C(9)–C(8)–H(8,1)	109 (2)	109 (2)
C(9)–C(8)–H(8,2)	110 (3)	109 (3)
H(8,1)–C(8)–H(8,2)	102 (4)	107 (4)
C(5)–C(9)–H(9,1)	111 (2)	108 (3)
C(5)–C(9)–H(9,2)	107 (3)	109 (2)
C(8)–C(9)–H(9,1)	111 (2)	114 (3)
C(8)–C(9)–H(9,2)	109 (2)	109 (2)
H(9,1)–C(9)–H(9,2)	107 (3)	102 (4)
N(6)–C(10)–H(10,1)	109 (4)	100 (3)
N(6)–C(10)–H(10,2)	119 (3)	113 (3)
N(6)–C(10)–H(10,3)	114 (3)	111 (2)
H(10,1)–C(10)–H(10,2)	93 (5)	112 (4)
H(10,1)–C(10)–H(10,3)	100 (4)	111 (4)
H(10,2)–C(10)–H(10,3)	117 (4)	109 (4)

Table 8. *Interatomic distances* (Å) *and angles* (°) *in the hydrogen bonds*

a	*b*	*c*	*ab*	*bc*	*ac*	*abc*
N(3′*B*)	–H	···N(6*A*)	0·81 (4)	1·99 (4)	2·790 (8)	169 (4)
N(1′*A*)	–H	···O(1*B*)	0·87 (4)	2·03 (4)	2·880 (6)	170 (3)
N(1′*B*)	–H	···O(1*A*)	0·95 (4)	2·01 (4)	2·914 (7)	158 (3)

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