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The Structure of N-(γ-Hydroxypropyl)granatanine-3-spiro-5'-hydantoin Monohydrate*†

BY J. VILCHES, F. FLORENCIO, P. SMITH-VERDIER AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, Madrid-6, Spain

Abstract. $C_{13}H_{21}N_3O_3 \cdot H_2O$, monoclinic, $P2_1/n$, $a = 12\cdot389$ (1), $b = 12\cdot108$ (1), $c = 9\cdot213$ (1) Å, $\beta = 93\cdot80$ (3)°, $Z = 4$, $V = 1378\cdot96$ (6) Å^3, $D_x = 1\cdot374$, $D_m = 1\cdot38$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·80625 mm^{-1}, $\lambda = 1\cdot5418$ Å. The structure was solved by direct methods and refined to $R = 0\cdot052$ for 2195 reflections. The bicyclo[3.3.1]nonane system adopts a boat–chair conformation. The resolution of the structure confirms the interpretation of IR spectra which showed the quaternary character of the piperidine N atom.

Introduction. Crystals of the title compound were supplied by Drs C. Avendaño and P. Ballesteros of the Departamento de Química Orgánica y Farmacéutica de la Facultad de Farmacia de la Universidad Complutense de Madrid. A crystal of dimensions 0·25 × 0·30 × 0·20 mm was used to measure the unit-cell parameters and the intensity data on a Philips PW 1100 automatic diffractometer fitted with a graphite-crystal monochromator. An ω–2θ scanning mode with Cu $K\alpha$ radiation was used to measure 2638 independent reflections with θ values below 65°; 2195 of these were considered as observed $[I > 2\sigma(I)$ where $\sigma(I)$ was determined from counting statistics]. The intensity data were reduced to structure factors and no absorption correction was applied.

The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 18 out of 20 atoms appeared on the E map calculated with 150 reflections. The two remaining atoms were located in a difference Fourier map. The structure was refined

by full-matrix least squares with isotropic and anisotropic thermal factors. All the H atoms, with the exception of the two water H atoms, were located in a difference map, and included only in one cycle of refinement with isotropic temperature factors. In successive cycles these temperature factors were kept fixed. The H atoms of the water were included at ideal positions in the first refinement and, in subsequent refinements, were kept fixed.

The refinement continued to a stage at which no parameter shift was significant. The final R value was 0·052 and $R_w = 0\cdot066$ where $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum |F_o|^2]^{1/2}$. A weighting scheme was applied so as to give no trends in $\langle w\Delta^2 \rangle$ *vs* $|F_o|$ and sin θ/λ. The expression for the function of the weighting scheme is given in Table 1 (Martínez-Ripoll & Cano, 1975). No trend in sin θ/λ was observed.

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).

Computations were carried out with programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970).

Table 1. *Function and coefficients for the weighting scheme*

$$w_T = K/[f(|F_o|)]^2, \quad 1/f(\sin \theta/\lambda); \quad K = 0\cdot673; \quad f(|F_o|) = a + b|F_o|.$$

	a	b
$|F_o| < 0\cdot12$	—	—
$0\cdot12 < |F_o| < 9\cdot53$	0·506	0·006
$9\cdot53 < |F_o| < 24\cdot38$	0·268	0·036
$24\cdot38 < |F_o|$	−0·647	0·065

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* The Conformation of Heterocyclic Spiro Compounds. X.

† Granatanine is 9-azabicyclo[3.3.1]nonane and hydantoin is 2,4-imidazolidinedione.

Table 2. *Atomic coordinates* (×10^4) *and thermal parameters* (×10^4) *for the non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j \cos (a_i, a_j).$$

	x	y	z	U_{eq} (Å^2)
C(1)	4031 (1)	3360 (1)	6287 (2)	303 (5)
C(2)	4567 (1)	2617 (1)	7491 (2)	302 (5)
C(3,5')	4580 (1)	1380 (1)	7106 (2)	251 (5)
C(4)	3477 (1)	1013 (1)	6426 (2)	293 (5)
C(5)	2977 (1)	1786 (1)	5238 (2)	292 (5)
C(6)	1927 (1)	2331 (2)	5645 (2)	391 (6)
C(7)	2101 (2)	3082 (2)	6953 (2)	435 (6)
C(8)	3003 (2)	3912 (2)	6743 (2)	396 (6)
N(9)	3787 (1)	2672 (1)	4935 (1)	272 (4)
C(10)	3465 (2)	3336 (2)	3596 (2)	410 (6)
C(11)	4404 (2)	3581 (2)	2718 (2)	537 (8)
C(12)	4121 (2)	4434 (3)	1557 (3)	715 (10)
N(1')	4906 (1)	718 (1)	8359 (2)	337 (5)
C(2')	5836 (1)	179 (1)	8164 (2)	302 (5)
N(3')	6237 (1)	429 (1)	6838 (2)	312 (4)
C(4')	5528 (1)	1108 (1)	6166 (2)	264 (5)
O(1)	6277 (1)	−459 (1)	9080 (1)	465 (5)
O(2)	5603 (1)	1518 (1)	4927 (1)	366 (4)
O(3)	3282 (1)	4120 (2)	558 (2)	706 (7)
O(4)	6702 (2)	3615 (2)	5713 (4)	1146 (12)

Table 3. *Atomic coordinates* (×10^3) *and thermal parameters* (×10^3) *for the H atoms with e.s.d.'s in parentheses*

$$U = \exp [-8\pi^2 U (\sin \theta/\lambda)^2].$$

	x	y	z	U (Å^2)
H(401)	655	292	563	34
H(402)	740	370	585	97
H(11)	455 (2)	393 (2)	599 (3)	19
H(21)	415 (2)	270 (2)	840 (2)	16
H(22)	532 (2)	286 (2)	775 (2)	11
H(41)	300 (2)	98 (2)	725 (2)	5
H(42)	356 (2)	27 (2)	604 (2)	8
H(51)	289 (2)	141 (2)	431 (2)	17
H(61)	140 (2)	174 (2)	582 (2)	21
H(62)	161 (2)	276 (2)	477 (3)	20
H(71)	143 (2)	350 (2)	712 (3)	33
H(72)	231 (2)	265 (2)	784 (3)	19
H(81)	275 (2)	447 (2)	600 (2)	15
H(82)	318 (2)	433 (2)	766 (3)	22
H(91)	448 (2)	225 (2)	476 (3)	24
H(101)	305 (2)	392 (2)	382 (2)	31
H(102)	289 (2)	286 (2)	301 (3)	45
H(111)	464 (3)	291 (3)	230 (4)	58
H(112)	505 (2)	389 (2)	339 (3)	53
H(121)	477 (4)	456 (4)	103 (4)	87
H(122)	358 (2)	507 (2)	157 (3)	24
H(301)	255 (5)	417 (5)	116 (6)	141
H(1')	457 (2)	66 (2)	912 (3)	17

Atomic coordinates are listed in Tables 2 and 3, bond lengths and angles in Table 4.*

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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 36138 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *and valence angles* (°) *with e.s.d.'s in parentheses for non-H atoms*

|			
C(1)—C(2)	1·543 (2)	C(7)—C(8)	1·525 (3)
C(1)—C(8)	1·522 (3)	N(9)—C(10)	1·504 (2)
C(1)—N(9)	1·513 (2)	C(10)—C(11)	1·490 (4)
C(2)—C(3,5')	1·540 (2)	C(11)—C(12)	1·511 (4)
C(3,5')—C(4)	1·531 (2)	C(12)—O(3)	1·395 (3)
C(3,5')—N(1')	1·442 (2)	N(1')—C(2')	1·347 (2)
C(3,5')—C(4')	1·541 (2)	C(2')—N(3')	1·383 (2)
C(4)—C(5)	1·538 (2)	C(2')—O(1)	1·243 (2)
C(5)—C(6)	1·528 (3)	N(3')—C(4')	1·326 (2)
C(5)—N(9)	1·507 (2)	C(4')—O(2)	1·254 (2)
C(6)—C(7)	1·514 (3)		
C(2)—C(1)—C(8)	112·7 (2)	C(1)—C(8)—C(7)	112·3 (2)
C(2)—C(1)—N(9)	108·9 (1)	C(1)—N(9)—C(5)	109·8 (1)
C(8)—C(1)—N(9)	110·1 (1)	C(1)—N(9)—C(10)	114·1 (1)
C(1)—C(2)—C(3,5')	114·3 (1)	C(5)—N(9)—C(10)	112·9 (1)
C(2)—C(3,5')—C(4)	110·7 (1)	N(9)—C(10)—C(11)	112·2 (2)
C(2)—C(3,5')—C(4')	110·9 (1)	C(10)—C(11)—C(12)	111·6 (2)
C(2)—C(3,5')—N(1')	111·3 (1)	C(11)—C(12)—O(3)	114·1 (2)
C(4)—C(3,5')—N(1')	111·2 (1)	C(3,5')—N(1')—C(2')	111·1 (1)
C(4)—C(3,5')—C(4')	113·7 (1)	N(1')—C(2')—N(3')	111·8 (2)
N(1')—C(3,5')—C(4')	98·5 (1)	N(1')—C(2')—O(1)	123·5 (2)
C(3,5')—C(4)—C(5)	114·9 (1)	N(3')—C(2')—O(1)	124·6 (2)
C(4)—C(5)—C(6)	113·4 (1)	C(2')—N(3')—C(4')	106·5 (1)
C(4)—C(5)—N(9)	108·9 (1)	C(3,5')—C(4')—N(3')	112·1 (1)
C(6)—C(5)—N(9)	109·1 (1)	C(3,5')—C(4')—O(2)	122·2 (1)
C(5)—C(6)—C(7)	112·1 (2)	N(3')—C(4')—O(2)	125·7 (2)
C(6)—C(7)—C(8)	111·2 (2)		
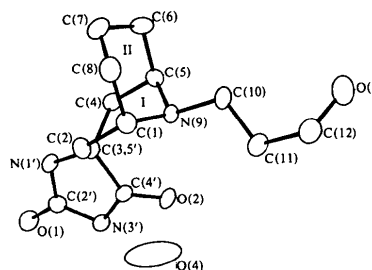
Fig. 1. The conformation of the molecule showing atom numbering.

Discussion. Fig. 1 shows the molecule with the numbering of the atoms.

The molecule contains two piperidine rings (I) and (II) joined by a common C—N—C bridge with a hydroxypropyl group attached to the N atom and a hydantoin ring substituted at the spiranic C(3,5').

The molecular symmetry (excepting the hydroxypropyl group) approximates to m [the mirror plane is defined by C(3,5'), N(9) and C(7)] since the opposed distances in the bicyclic system and the distances of corresponding atoms to the plane are very similar.

According to several authors (Brown, Eglinton, Martin, Parker & Sim, 1964; Webb & Becker, 1967) simple [3.3.1]nonane compounds in which both three-C-atom bridges are fully saturated adopt a chair–chair conformation in which, in order to increase the non-bonded C(3)···C(7) distance, the cyclohexane rings are distinctly flattened, with ring valence angles at

C(2), C(3), C(4), C(6), C(7) and C(8) rather greater than the tetrahedral value. On the other hand, Tamura & Sim (1968) in 9-benzoyl-3α-bromo-2β-hydroxy-9-azabicyclo[3.3.1]nonane and, more recently, Florencio, Smith-Verdier & Garcia-Blanco (1978) in *N*-(β-hydroxyethyl)granatanine-3-spiro-5'-hydantoin found a boat–chair conformation. In the present compound the bicyclic system also adopts a boat–chair conformation, possibly due to the bulky hydantoin ring attached to the spiranic C(3,5') atom. The displacements of C(3,5') and N(9) from the least-squares plane through C(1), C(2), C(4) and C(5) (Table 5) are 0·568 and 0·732 Å respectively; consequently the C(1), C(2), C(3,5'), C(4), C(5) part of the boat is somewhat flattened. This flattening could be produced by the interaction N(9)–H···O(2) of 2·648 Å, a slightly short hydrogen bond. Table 6 lists torsion angles.

The non-bonded N(9)···C(3,5') distance of 2·674 Å is similar to that found in *N*-(β-hydroxyethyl)-granatanine-3-spiro-5'-hydantoin and therefore larger than the corresponding distance in an ideal boat (2·56 Å) (Webb & Becker, 1967).

The quaternization of the piperidinic N(9) is produced by proton transfer from the N(3')–H group to N(9). Consequently a 'zwitterion' structure is

present. This structure is stabilized by the water molecule. Bond lengths and angles in the bicyclic system are in good agreement with those found in the literature; however, in the hydantoin ring a shortening in N(3')–C(2') and N(3')–C(4') and an increase in C(2')–O(1) and C(4')–O(2) are observed, indicating noticeable conjugation in the (O≗C≗N≗C≗O)⁻ bond system.

There are five crystallographically independent hydrogen bonds in the crystal structure, one of them intramolecular: N(9)–H···O(2). Hydrogen bonds between water molecules are indicated by O(2)···O(4) and O(1)···O(4) distances of 2·948 (3) and 2·738 (3) Å respectively. The intricate three-dimensional network in which the molecules are hydrogen bonded is shown in Fig. 2 which is a projection of the structure along **c**. Table 7 shows the geometry of the hydrogen bonds.
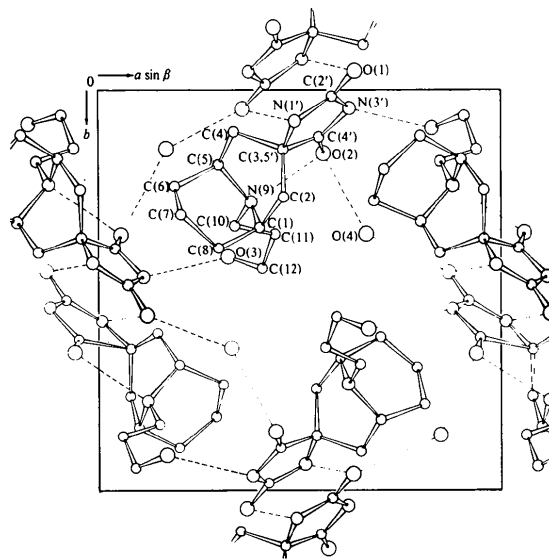
Table 6. *Torsion angles* (°)

C(8) C(1)– N(9)–C(5)	−60·5 (2)		C(3,5') C(4)–C(5)– N(9)	6·1 (2)
C(2) C(1) N(9)–C(5)	63·5 (2)		C(4) C(5) N(9)–C(1)	−62·6 (2)
N(9) C(1)–C(8) C(7)	55·1 (2)		C(6)–C(5) N(9)–C(1)	61·6 (2)
N(9)–C(1) C(2)–C(3,5')	−7·7 (2)		N(9) C(5)–C(6) C(7)	−58·0 (2)
C(1)–C(2) C(3,5')–C(4)	−45·1 (2)		C(5) C(6) C(7)–C(8)	52·5 (2)
C(2) C(3,5')–C(4) C(5)	46·2 (2)		C(6)–C(7)–C(8)–C(1)	−51·0 (2)

Table 5. *Equations of some least-squares planes and distances* (Å) *of atoms from them, with e.s.d.'s in parentheses*

X,Y,Z are coordinates in Å with respect to orthogonal axes.

Plane 1: C(3,5'), N(1'), C(2'), N(3'), C(4')
$$-0{\cdot}4837X - 0{\cdot}7758Y - 0{\cdot}4052Z = -6{\cdot}4759$$
Plane 2: C(1), C(2), C(4), C(5)
$$0{\cdot}7811X - 0{\cdot}2174Y - 0{\cdot}5853Z = -0{\cdot}6607$$
Plane 3: C(1), C(5), C(6), C(8)
$$-0{\cdot}0277X + 0{\cdot}4723Y - 0{\cdot}8810Z = -3{\cdot}3062$$
Plane 4: C(3,5'), C(7), N(9)
$$-0{\cdot}5013X - 0{\cdot}7717Y - 0{\cdot}3913Z = -6{\cdot}4725$$

	Plane 1	Plane 2	Plane 3	Plane 4
C(1)	–	−0·005 (2)	0·008 (2)	−1·240 (2)
C(2)	–	0·005 (2)	–	−1·275 (2)
C(3,5')	−0·002 (2)	0·568 (2)	–	0·000 (2)
C(4)	–	−0·005 (2)	–	1·251 (2)
C(5)	–	0·004 (2)	−0·008 (2)	1·230 (2)
C(6)	–	–	0·011 (2)	1·240 (2)
C(7)	–	–	−0·623 (2)	0·000 (2)
C(8)	–	–	−0·009 (2)	−1·267 (2)
N(9)	–	0·732 (1)	0·716 (1)	0·000 (1)
N(1')	−0·005 (2)	–	–	0·004 (2)
C(2')	0·011 (2)	–	–	−0·006 (2)
N(3')	−0·009 (1)	–	–	−0·052 (1)
C(4')	0·007 (2)	–	–	−0·026 (2)
O(1)	0·032 (2)	–	–	0·015 (2)
O(2)	0·003 (1)	–	–	−0·048 (1)
C(10)	–	–	–	0·020 (2)
C(11)	–	–	–	−0·503 (3)
C(12)	–	–	–	−0·742 (3)
O(3)	–	–	–	0·401 (2)

Fig. 2. The structure viewed along **c**.

Table 7. *Geometry of the hydrogen bonds*

			ab (Å)	*bc* (Å)	*ac* (Å)	*abc* (°)
a	*b*	*c*				
N(9)–H···O(2ⁱ)			1·03 (2)	1·64 (2)	2·648 (2)	166 (2)
N(1')–H···O(1ⁱⁱ)			0·84 (2)	2·04 (2)	2·876 (2)	178 (2)
O(3)–H···N(3'ⁱⁱⁱ)			1·10 (6)	1·85 (6)	2·916 (2)	165 (5)
O(4)–H···O(2ⁱ)			0·87	2·14	2·948 (3)	155
O(4)–H···O(1ⁱᵛ)			0·87	1·93	2·738 (3)	155

Symmetry code: (i) *x,y,z*; (ii) −*x* + 1, −*y*, −2 + *z*; (iii) *x* − ½, −*y*, *z* − ½; (iv) −*x* + ½, *y* + ½, −*z* + ½.

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Perchloro(9-phenyl-3-fluorenone). A Disordered Structure

BY X. SOLANS, C. MIRAVITLLES AND F. PLANA

UEI de Difracción de Rayos-X y Estructuras Cristalinas, Instituto 'Jaime Almera' del CSIC, Egipciacas 15, Barcelona-1, Spain

AND J. P. DECLERCQ* AND G. GERMAIN

Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain, 1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

Abstract. $C_{19}Cl_{12}O$, $M_r = 669.64$, $F(000) = 1304$, monoclinic, $C2/c$, $a = 16.420$ (4), $b = 15.005$ (3), $c = 10.478$ (3) Å, $\beta = 119.36$ (2)°, $V = 2250.0$ (9) Å^3, $Z = 4$, $D_c = 1.97$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.7107$ Å, $\mu = 1.48$ mm^{-1}. Direct methods were used to determine the structure from X-ray data. Block-diagonal least-squares refinement based on 1419 reflections converged with R at 0.045 and with occupation factors for the Cl(14) and O(14) atoms equal to 0.5. The molecule is located at a special position (twofold axis) and is slightly distorted as a consequence of steric interactions between Cl atoms.

Introduction. The success achieved in the synthesis of functionalized radicals of the perchloro(triphenylmethyl) free-radical series (Ballester, Riera, Castañer, Badía & Monsó, 1971) and their bonding to molecules of biological interest (Ballester, Riera, Rodriguez & Rovira, 1977; Ballester, Castañer, Riera & Veciana, 1978) prompted Ballester and co-workers to try the same functionalization in fluorene radicals; for this reason, the title compound was synthesized as the first step towards obtaining these radicals.

Perchloro(9-phenyl-3-fluorenone) (PPF) is obtained together with its isomer perchloro[4-(9-fluorenylidene)-2,5-cyclohexadien-1-one] and with the free radical 9-phenyl-9-fluorenyl which is one of the original products in the synthesizing process (Armet, 1978). In order to make a decisive confirmation of the structural hypotheses established by means of spectral and chemical techniques by the aforementioned authors, the structure of PPF was determined by X-ray diffraction methods.

Irregular black crystals were obtained by evaporation in chloroform. Initially a crystal $0.2 \times 0.2 \times 0.2$ mm was selected and an attempt to determine its structure was made without success. A second crystallization (also by evaporation in chloroform), but slower and more controlled, produced new black crystals with a more defined habit and of generally better quality, and so a second crystal was chosen ($0.2 \times 0.2 \times 0.3$