

3-Ethyl-3-azabicyclo[3.2.1]octane-8-spiro-5'-hydantoin*

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

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

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Abstract. $C_{11}H_{17}N_3O_2$, monoclinic, $P2_1/c$, $a = 6.527(1)$, $b = 12.337(1)$, $c = 14.923(1)$ Å, $\beta = 114.30(1)^\circ$, $Z = 4$, $D_x = 1.208$, $D_m = 1.2$ Mg m $^{-3}$, $\mu = 0.094$ mm $^{-1}$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å. The molecule contains a bicyclo system which assumes a chair-envelope conformation.

Introduction. The compound was prepared by Dr Galvez of the Facultad de Farmacia de la Universidad Complutense de Madrid.

The intensities were collected from a crystal $0.30 \times 0.45 \times 0.32$ mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ mode with Mo $K\alpha$ radiation monochromatized by a graphite crystal. 3094 independent reflexions were measured of which 2303 had $I > 2\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. The systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ uniquely determine the space group as $P2_1/c$. Intensities were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) with the 200 largest E values. An E map gave all the heavy atoms. Refinement was by full-matrix least squares.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1$. H atoms were located from a difference map, and assigned isotropic thermal parameters. The final refinement included all atomic parameters and gave $R = 0.072$. A final difference map had no significant peaks. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Tables 1 and 2.†

Discussion. Interatomic distances and angles are given in Fig. 1. A projection of the structure down b with the atomic numbering is shown in Fig. 2.

The molecule consists of a piperidine ring with an ethyl group attached to the N, and a five-membered ring joined to the former by a common C—C bridge whose central atom is the spiranic C to which the hydantoin ring is attached. Table 3 lists the torsion angles.

The piperidine ring adopts a distorted-chair conformation with approximate mirror symmetry [C_s plane through C(3,5') and N(6)] with $\Delta C_s^{(3,5')} = 0.29$,

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34411 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The Conformation of Heterocyclic Spiro Compounds. VI.

Table 1. Positional parameters for the heavy atoms

	x	y	z
C(1)	0.8876 (4)	0.0839 (1)	0.8533 (1)
C(2)	1.0041 (4)	0.1555 (1)	0.9436 (1)
C(3,5')	0.8263 (3)	0.1948 (1)	0.9791 (1)
C(4)	0.6960 (4)	0.2742 (1)	0.8945 (1)
C(5)	0.5664 (4)	0.2079 (2)	0.8020 (1)
N(6)	0.7182 (3)	0.1450 (1)	0.7711 (1)
C(7)	1.0865 (4)	0.2616 (2)	0.9150 (2)
C(8)	0.8847 (4)	0.3407 (1)	0.8849 (2)
C(9)	0.5813 (5)	0.0717 (2)	0.6906 (2)
C(10)	0.7191 (6)	0.0023 (2)	0.6521 (2)
N(1')	0.6899 (3)	0.1123 (1)	0.9979 (1)
C(2')	0.6713 (4)	0.1270 (1)	1.0838 (1)
N(3')	0.8101 (3)	0.2136 (1)	1.1319 (1)
C(4')	0.9210 (4)	0.2541 (1)	1.0781 (1)
O(1)	0.5593 (3)	0.0742 (1)	1.1166 (1)
O(2)	1.0608 (3)	0.3245 (1)	1.1049 (1)

Table 2. Positional parameters for the hydrogen atoms

	x	y	z
H(11)	0.817 (5)	0.018 (2)	0.868 (2)
H(12)	1.005 (5)	0.059 (2)	0.834 (2)
H(2)	1.121 (5)	0.115 (2)	0.993 (2)
H(4)	0.584 (6)	0.319 (2)	0.910 (2)
H(51)	0.477 (5)	0.256 (2)	0.746 (2)
H(52)	0.452 (6)	0.156 (2)	0.812 (2)
H(71)	1.132 (5)	0.251 (2)	0.862 (2)
H(72)	1.215 (6)	0.291 (3)	0.969 (2)
H(81)	0.920 (6)	0.407 (2)	0.930 (3)
H(82)	0.843 (6)	0.367 (2)	0.818 (2)
H(91)	0.471 (6)	0.115 (2)	0.635 (2)
H(92)	0.483 (7)	0.024 (2)	0.713 (2)
H(101)	0.789 (6)	-0.059 (2)	0.698 (2)
H(102)	0.831 (10)	0.041 (3)	0.643 (4)
H(103)	0.626 (7)	-0.032 (3)	0.588 (3)
H(1')	0.616 (6)	0.063 (3)	0.963 (2)
H(3')	0.807 (7)	0.245 (3)	1.185 (3)

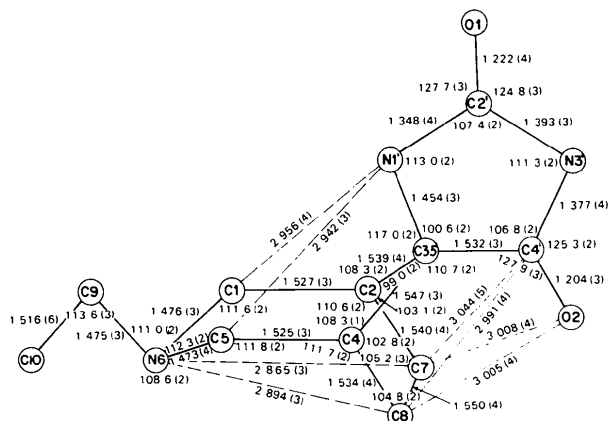


Fig. 1. Bond lengths (Å) and angles (°) involving the non-hydrogen atoms. Angles not shown: $C(4)-C(3,5')-N(1') = 115.2(2)$, $C(2)-C(3,5')-C(4') = 114.9(2)^\circ$.

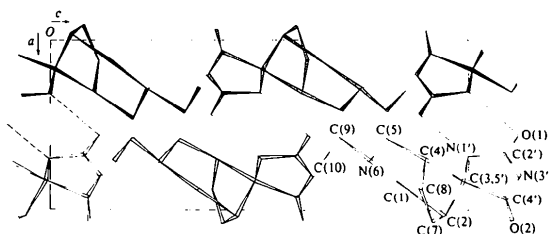


Fig. 2. Projection of the structure along *b*.

$\Delta C_2^{2-3,5} = 7.84$ and $\Delta C_2^{1-2} = 21.70^\circ$ (Duax & Norton, 1975). The deviations of $C(3,5')$ and $N(6)$ from the plane through the remaining atoms (Table 4) of the piperidine ring are $-0.897(3)$ and $0.575(3)$ Å respectively; consequently the part of the ring opposite to the spiranic $C(3,5')$ is flattened. This flattening could be due to the steric interaction between the $C(7)-C(8)$ ethylene bridge and $N(6)$. This interaction is clearly reflected in the $C(7)\cdots N(6)$ and $C(8)\cdots N(6)$ non-bonded separations of $2.865(3)$ and $2.894(3)$ Å respectively and in the significantly small angle $C(2)-C(3,5')-C(4)$ of $99.0(2)^\circ$.

The five-membered ring adopts a $C(3,5')$ -envelope conformation. This conformation has been studied in terms of the torsion angles (Altona, Geise & Romers, 1968). The pseudo-rotation parameters Δ and φ are -31.4 and 49.7° respectively. The deviations of atoms from the plane through $C(2)-C(4)$, $C(7)-C(8)$ are given in Table 4.

The configuration of $N(6)$ is pyramidal as in *N*-methyltropene-3-spiro-5'-hydantoin (Smith-Verdier, Florencio & García-Blanco, 1977) but the substituent ethyl group is in an equatorial position.

In the hydantoin ring, bond lengths and angles are in good agreement with those in *N*-methylgranatanine-3-spiro-5'-hydantoin (Florencio, Smith-Verdier & García-Blanco, 1978a) and *N*-(β -hydroxyethyl)granatanine-3-

Table 3. Torsion angles (°) involving non-hydrogen atoms

The sign convention is as defined by Klyne & Prelog (1960).

$C(1)-C(2)-C(3,5')-C(4)$	$-70.7(2)$
$C(2)-C(3,5')-C(4)-C(5)$	$70.5(2)$
$C(3,5')-C(4)-C(5)-N(6)$	$-62.4(3)$
$C(4)-C(5)-N(6)-C(1)$	$48.8(2)$
$C(5)-N(6)-C(1)-C(2)$	$-48.9(3)$
$N(6)-C(1)-C(2)-C(3,5')$	$62.8(3)$
$C(2)-C(3,5')-C(4)-C(8)$	$-47.9(2)$
$C(3,5')-C(4)-C(8)-C(7)$	$31.1(2)$
$C(4)-C(8)-C(7)-C(2)$	$-2.0(2)$
$C(8)-C(7)-C(2)-C(3,5')$	$-28.0(2)$
$C(7)-C(2)-C(3,5')-C(4)$	$46.5(2)$

Table 4. Some least-squares planes and deviations (Å) of individual atoms from them

Atoms marked with asterisks were used to define the planes.

	Plane 1	Plane 2	Plane 3
$C(1)$	$-0.833(3)$	$-0.001(3)^*$	$1.413(3)$
$C(2)$	$-0.930(3)$	$0.001(3)^*$	$0.007(3)^*$
$C(3,5')$	$0.063(3)^*$	$-0.897(3)$	$-0.742(3)$
$C(4)$	$1.386(3)$	$-0.001(3)^*$	$0.007(3)^*$
$C(5)$	$1.585(3)$	$0.001(3)^*$	$1.427(3)$
$N(6)$	$0.509(3)$	$0.575(3)$	$2.176(2)$
$C(7)$	$-0.399(3)$	$1.390(3)$	$0.013(3)^*$
$C(8)$	$1.125(3)$	$1.375(3)$	$-0.013(3)^*$
$C(9)$	$0.662(3)$	$0.366(3)$	$3.459(3)$
$C(10)$	$-0.391(4)$	$0.920(4)$	$4.328(4)$
$N(1')$	$-0.039(3)^*$	$-2.255(3)$	$-0.754(3)$
$C(2')$	$-0.001(3)^*$	$-3.178(3)$	$-1.974(2)$
$N(3')$	$0.001(1)^*$	$-2.516(3)$	$-2.873(1)$
$C(4')$	$-0.055(3)^*$	$-1.170(3)$	$-2.244(2)$
$O(1)$	$0.001(2)$	$-4.382(2)$	$-2.275(2)$
$O(2)$	$-0.144(2)$	$-0.378(2)$	$-2.793(2)$

$$\text{Plane 1: } -0.647X + 0.632Y - 0.426Z = -3.813$$

$$\text{Plane 2: } 0.667X + 0.548Y - 0.505Z = -4.919$$

$$\text{Plane 3: } -0.091X - 0.315Y - 0.945Z = 12.652$$

Angles between planes (°)

$$\text{Plane 1-2} = 82.5$$

$$\text{Plane 1-3} = 81.7$$

$$\text{Plane 2-3} = 68.6$$

spiro-5'-hydantoin (Florencio, Smith-Verdier & García-Blanco, 1978b).

The molecular packing as viewed along *b* is shown in Fig. 2. Hydrogen bonds of types $N-H\cdots O$ and $N-H\cdots N$ link the molecules together. Two $N(1')(-x+1, -y, -z+2)-H\cdots O(1)(x, y, z)$ bonds of length $2.927(3)$ Å with $N(1')-H\cdots O(1)$ angles of $176(3)^\circ$ are formed between pairs of molecules related by a centre of symmetry while the $N(3')(x, \frac{1}{2}-y, \frac{1}{2}+z)\cdots N(6)(x, y, z)$ bond of length $2.957(3)$ Å and $N(3')-H\cdots N(6)$ angle of $160(3)^\circ$ link the molecules forming chains along *a*. The other intermolecular contacts correspond to normal van der Waals interactions.

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7,11-Bis(5-methyl-2-furyl)spiro[5.5]undecane-1,5,9-trione

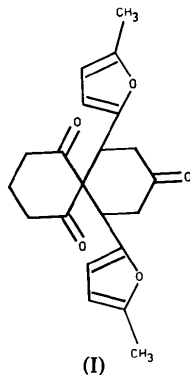
BY H. KRABBENDAM AND A. L. SPEK

Laboratorium voor Structuurchemie, Rijksuniversiteit Utrecht, Transitorium III, Padualaan 8, Utrecht, The Netherlands

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Abstract. $C_{21}H_{22}O_5$, $M_r = 354.43$, orthorhombic, $P2_12_12_1$, $a = 9.052$ (4), $b = 10.439$ (6), $c = 19.561$ (2) Å, $V = 1848.5$ Å³, $Z = 4$, $D_m = 1.25$, $D_x = 1.273$ Mg m⁻³, $R_F = 0.041$ for 1736 reflections. The cyclohexanone ring has the twist-boat configuration.

Introduction. Crystals of the title compound (I) were provided, as a racemic mixture, by Professor H. Wynberg and Dr W. ten Hoeve, University of Groningen. The structure determination was undertaken to confirm the proposed twisted conformation of the cyclohexanone ring. A colourless transparent block-shaped crystal $0.20 \times 0.33 \times 0.61$ mm was investigated on an Enraf–Nonius CAD-4 diffractometer to obtain cell dimensions. The space group is



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uniquely determined by the observed extinctions $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, $00l$ for $l = 2n + 1$ to be $P2_12_12_1$. Diffraction intensities were collected up to $\theta = 27.5^\circ$ with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Lorentz and polarization corrections but none for absorption were applied ($\mu = 0.098$ mm⁻¹). 2415 intensities were measured; 1736 with $I > 2\sigma(I)$ were included in the refinement.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and by a subsequent cycle of structure factor and Fourier calculations. The structure was refined by a block-diagonal least-squares procedure. 15 H atoms were found in the difference map, the other 7 were placed at calculated positions, and refined with isotropic temperature factors fixed at $U_{iso} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$, with U 's of bonded C atoms. The final R_F and R_{wF} were 0.041 and 0.055 respectively. Cromer & Mann's (1968) analytical scattering factors for O and C were used. Those for H were taken from Stewart, Davidson & Simpson (1965). A Dutch version of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for most calculations.

The positional parameters are listed in Tables 1 and 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34412 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.