

MOLECULAR STRUCTURE OF 3,7-BIS(β -OXYETHYL)-9,9-DIMETHYL- 1,5-DINITRO-3,7-DIAZABICYCLO[3.3.1]NONANE

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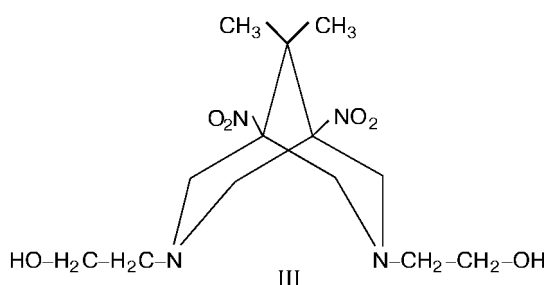
UDC 548.737

Many 3,7-diazabicyclo[3.3.1]nonanes have a double chair conformation, and only some of these compounds having certain groups in a molecule exist as chair-boat forms. Thus 3,7-diazabicyclo[3.3.1] nonanes with alkyl groups at the nitrogen atoms and a ketone group in the 9 position of the diazabicyclononane ring (I) [1-3] or a ketone group in the side chain outside the ring in diazabicyclononane (II) [4] have a chair-boat conformation. This is caused by the interaction of the ketone and NR groups which are in the β -position relative to each other; the absence of one of these groups leads to a double chair conformation (Scheme in [4]).

It was interesting to find out whether replacement of the ketone group by another electron-accepting group can lead to an analogous interaction stabilizing the chair-boat conformation.

The aim of the present work is a molecular structure determination for 3,7-diazabicyclo[3.3.1]nonane, which, unlike diazabicyclononanes I and II, has an NO₂ group instead of a ketone group in the β -position relative to the NR groups.

For this purpose, we have performed an X-ray diffraction analysis of 3,7-bis(β -hydroxyethyl)-9,9-dimethyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane (III). The 3,7- β -hydroxyethyl groups were introduced instead of the necessary alkyl ones because of better crystallization of the above diazabicyclononane. Synthesis of the compound is described in [5].



Crystals suitable for an XRD analysis were grown from an aqueous solution.

The triclinic cell parameters were determined on an Enraf-Nonius CAD-4 four-circle automatic diffractometer and refined using 24 reflections: $a = 8.054(2)$, $b = 9.569(2)$, $c = 11.124(2)$ Å, $\alpha = 80.75(3)$, $\beta = 77.38(3)$, $\gamma = 78.28(3)^\circ$, $V = 813.1(3)$ Å³, $M = 362.5$, $d_{\text{calc}} = 1.358$ g/cm³, $Z = 2$. The intensities of 1297 independent reflections with $I > 2\sigma(I)$ were collected on the same diffractometer (λ MoK α , $\omega/2\theta$ scan mode, graphite monochromator, $\theta_{\text{max}} = 26^\circ$, space group $P\bar{1}$).

The structure was solved by direct methods and refined by the least-squares procedure in an anisotropic approximation for nonhydrogen atoms. The H atoms were located geometrically, and included in the least-squares refinement using isotropic thermal parameters. All structure calculations were carried out with SHELXL-93. The final R index was $R = 0.065$ for 1297 reflections with $I > 2\sigma(I)$. The atomic coordinates are listed in Table 1. Tables 2 and 3 give the bond lengths and angles. The relatively high R index is explained by the poor quality of the crystal chosen for the experiment.

The X-ray structure analysis unambiguously shows that compound III has a chair-chair conformation. On the other hand, the hydroxyl groups of the β -hydroxyethyl residues at N(3) and N(7) are close to each other (Fig. 1), probably, as

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TABLE 1. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) (\AA^2)

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
O1	−2417(6)	2102(6)	2839(6)	124(2)	N7	1782(6)	2483(6)	4176(4)	651(15)
O2	−2104(6)	3809(7)	1383(6)	104(2)	C8	3188(9)	1619(8)	3420(6)	63(2)
O3	5488(6)	1551(5)	0351(5)	85(2)	C9	1546(6)	1894(6)	1653(5)	487(14)
O4	5222(6)	−0085(5)	1849(4)	89(2)	C10	1191(12)	0357(9)	1982(11)	78(3)
O5	3577(8)	6131(7)	3698(6)	118(2)	C11	1594(10)	2273(10)	0266(7)	70(2)
O6	3156(9)	3898(9)	5696(6)	128(2)	N12	−1603(6)	2963(6)	2224(6)	72(2)
C1	3223(6)	2083(5)	2040(5)	455(14)	N13	4778(6)	1108(5)	1355(5)	547(13)
C2	3584(7)	3626(6)	1630(7)	55(2)	C14	2529(9)	6115(7)	1871(9)	69(2)
N3	2198(5)	4649(4)	2237(4)	533(13)	C15	3937(11)	6382(8)	2408(7)	73(2)
C4	0524(7)	4514(7)	2046(8)	61(2)	C16	1701(13)	2050(13)	5500(8)	94(3)
C5	0208(6)	2969(6)	2457(5)	54(2)	C17	3116(13)	2433(11)	5944(8)	98(3)
C6	0122(8)	2508(9)	3832(6)	69(2)					

TABLE 2. Bond Lengths $d(\sigma)$ (\AA)

Bond	$d(\sigma)$	Bond	$d(\sigma)$	Bond	$d(\sigma)$	Bond	$d(\sigma)$
O1N12	1.191(6)	O2N12	1.218(6)	N12C5	1.537(7)	N13C1	1.535(6)
O3N13	1.192(6)	O4N13	1.205(5)	C11C9	1.520(9)	C10C9	1.527(9)
O5C15	1.391(8)	O6C17	1.390(10)	C9C1	1.556(7)	C9C5	1.563(7)
N3C4	1.444(7)	N3C2	1.450(7)	C5C6	1.513(8)	C5C4	1.531(8)
N3C14	1.458(8)	N7C8	1.449(8)	C1C8	1.523(8)	C1C2	1.540(7)
N7C16	1.456(9)	N7C6	1.464(8)	C14C15	1.473(10)	C16C17	1.467(12)

TABLE 3. Bond Angles $\omega(\sigma)$ (deg)

Angle			$\omega(\sigma)$	Angle			$\omega(\sigma)$
C4	N3	C2	112.5(5)	C4	N3	C14	111.7(5)
C2	N3	C14	111.2(5)	C8	N7	C16	112.8(6)
C8	N7	C6	111.7(5)	C16	N7	C6	111.1(6)
O1	N12	O2	123.3(6)	O1	N12	C5	118.8(6)
O2	N12	C5	117.9(6)	O3	N13	O4	122.4(5)
O3	N13	C1	119.0(5)	O4	N13	C1	118.6(5)
C11	C9	C10	106.4(7)	C11	C9	C1	112.8(5)
C10	C9	C1	112.7(5)	C11	C9	C5	113.6(5)
C10	C9	C5	112.3(6)	C1	C9	C5	99.0(4)
C6	C5	C4	113.5(6)	C6	C5	N12	105.7(4)
C4	C5	N12	105.5(5)	C6	C5	C9	112.1(5)
C4	C5	C9	111.1(5)	N12	C5	C9	108.5(4)
C8	C1	N13	106.1(4)	C8	C1	C2	112.6(5)
N13	C1	C2	105.5(4)	C8	C1	C9	111.9(5)
N13	C1	C9	109.3(4)	C2	C1	C9	111.0(5)
N3	C2	C1	110.4(5)	N3	C4	C5	110.3(5)
N7	C6	C5	110.9(5)	N7	C8	C1	111.6(5)
N3	C14	C15	112.0(7)	O5	C15	C14	111.5(7)
N7	C16	C17	112.4(7)	O6	C17	C16	112.2(8)

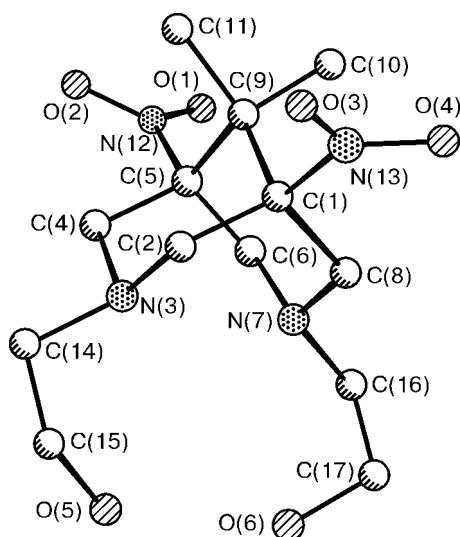


Fig. 1. Molecular structure with an atomic numbering scheme.

a result of hydrogen bonding. This interaction evidently stabilizes the double chair conformation, much as the N(3)...N(7) interaction does in 3,7-diazabicyclo[3.3.1]nonan-9-one [3, 6].

An additional X-ray diffraction study is required to answer the question whether the replacement of the keto group by the NO₂ group stabilizes the chair-boat conformation in 3,7-diazabicyclo[3.3.1]nonanes.

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