The Structure of New *cis* and *trans* 3'-Phenyl-3',3a',4',5',6',7a'-hexahydro-2,1-benzisoxazole-7a'-spiro-2-(3-phenylaziridine)

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The reaction of dibenzalcyclohexanone with hydroxylamine hydrochloride afforded three compounds **1-3** including the aziridine **3** showing a 3',3a'-*trans* configuration. Now we report on the isolation of a new aziridine **4**, possessing a 3',3a'-*cis* configuration. Its structure was deduced by 2D nmr and single crystal X-ray diffraction studies.

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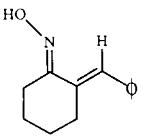
Introduction.

It is known that the reaction of α,β-unsaturated ketones with hydroxylamine results in the formation of highly complicated mixtures of products [1]. Recently, we have described the reaction between dibenzalacetone and hydroylamine hydrochloride that leads to new piperidinone oximes when performed under phase transfer conditions [2]. On the other hand, the reaction of dibenzalcyclohexanone with hydroxylamine hydrochloride and potassium hydroxide in refluxing ethanol afforded three compounds: the oxime of 2-benzylidenecyclohexanone (**1**), 3-phenyl-7-benzylidene-3,3a,4,5,6,7-hexahydro-2,1-benzisoxazole (**2**) and 3'-phenyl-3',3a',4',5',6',7a'-hexahydro-2,1-benzisoxazole-7a'-spiro-2-(3-phenylaziridine) (**3**) [3]. The spiroaziridine structure **3** was established by 2D nmr and X-ray crystallographic analysis as the 3',3a'-*trans* isomer. The unresolved question was why only the 3',3a'-*trans*-isomer was obtained. Now, we report on the isolation of the 3',3a'-*cis* isomer **4**, from the crude reaction mixture (residual fractions). The purification of that aziridine presented a challenge in itself; as it forms a mixture difficult to separate from the oxime **1**. In order to purify compound **4**, we have performed a novel treatment using silver oxide and ultrasounds. The nmr features of **4** differ considerably from those of its isomer **3**. The structure of the title spiroaziridine was deduced by 2D nmr [4,5] and its stereochemistry was confirmed by single crystal X-ray diffraction.



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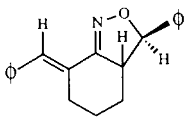

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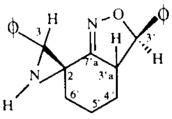

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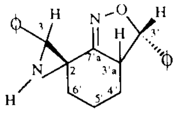

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Results and Discussion.

The mass spectrum of compound **4** was identical to that reported for **3** [3]. The ^{1}H nmr spectra of compounds **3** and **4** are presented in Figure 1 and their proton and carbon chemical shifts are given in Table 1. The coupling constants between H-3' and H-3'a in both isomers **3** and **4** have similar values 12.0 and 11.1 Hz respectively. However, the aziridine **4** displays several nmr features related to the chemical shifts of H-4'ax, H-4'eq, H-6'ax and H-6'eq, that differ from those observed for aziridine **3**. Product **4** shows a doublet at δ_H 5.831 assigned to the H-3' proton and resulting from the coupling with H-3'a (^3J = 11.1 Hz). The use of the Karplus theoretical calculation [6] did not allow to distinguish the *cis*/*trans* attachment of phenylisoxazole moiety using *e.g.* the vicinal coupling constants.

The second approach to configurational assignment in cyclohexanes as well as in other rings was to make use of the differential shielding of axial (pseudoaxial) and equatorial (pseudoequatorial) substituents arising from the magnetic

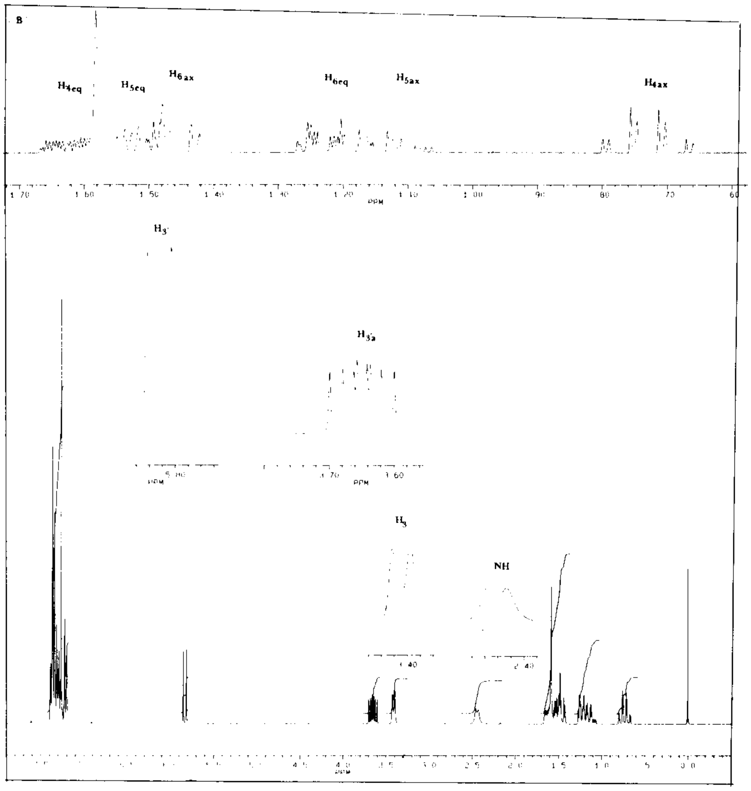

Figure 1. A) 400-MHz ^1H nmr spectrum of **3**, B) 300-MHz ^1H nmr spectrum of **4**.

Table 1

^1H and ^{13}C Chemical Shifts and Coupling Constants (Hz) of **3** and **4** [a]

	3			**4**		
Position	δ_H	J	δ_C	δ_H	J [b]	δ_C [c]
2			40.5			40.8
3	3.420 bs		47.6	3.415 b	0.7 (3, 6'a)	47.7
3'	5.157 d	12.0 (3', 3'a)	89.9	5.831 d	11.1 (3', 3'ax)	85.0
3'a	3.218 dt	12.0 (3'a, 4'ax), 6.5 (3'a, 4'eq)	56.2	3.650 ddd	12.7 (3'a, 4'ax), 6.15 (3'a, 4'eq)	52.6
4'eq	2.155 m		29.6	1.630 m	-13.1 (4'eq, 4'ax), 3.45 (4'eq, 5'eq)	26.5
4'ax	1.522 dq	-12.5 (4'ax, 4'eq), 3.5 (4'ax, 5'eq)		0.720 m	13.2 (4'ax, 5'ax), 3.20 (4'ax, 5'eq)	
5'eq	1.660 qd	-13.5 (5'eq, 5'ax), 3.5 (5'eq, 6'eq)	22.8	1.500 m	-13.9 (5'eq, 5'ax), 3.10 (5'eq, 6'eq)	22.8
5'ax	1.172 tq	13.5 (5'ax, 6'ax), 3.5 (5'ax, 4'eq)		1.143 m	13.5 (5'ax, 6'ax), 3.20 (5'ax, 4'eq)	
6'eq	1.319 td	-13.5 (6'eq, 6'ax), 3.5 (6'eq, 5'ax)	27.9	1.230 m	3.4 (6'eq, 5'ax), 1.50 (6'eq, 4'eq)	27.4
6'ax	1.739 dt	13.5 (6'ax, 5'ax), 4.0 (6'ax, 5'eq)		1.480 m	-13.9 (6'ax, 6'eq), 3.85 (6'ax, 5'eq)	
7'a			163.2			161.1
NH	2.418 bs			2.430 bs		
Phenyls	7.410		138.6	7.210		137.9
	7.350		135.7	7.350		136.0
	8.270		128.8			128.4
			128.5			128.2
			128.1			127.9
			127.8			127.4
			127.4			126.0
			126.1			

[a] Varian XL-400 s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. [b] Confirmed by double quantum filtered COSY and spectral simulations. [c] From DEPT 135, DEPT 90 and HECTOR $^1J_{C-H}$.

Table 2

Observed ^{1}H-^{1}H Connectivities from HOMOCOSY Experiments and ^{1}H-^{13}C Connectivities from HECTOR Experiments on 4 [a]

Proton	δ_H	^{1}H connectivities [b]	δ_C connectivities
H-3'	5.831	H-3'a	85.0
H-3'a	3.650	H-3', H-4'eq, H-4'ax	52.6
H-4'eq	1.630	H-3'a, H-4'ax, H-5'eq, H-5'ax	26.5
H-6'ax	1.480	H-5-ax, H-6'eq	27.4
H-6'eq	1.230	H-5'eq, H-6'ax, H-5'ax	27.4
H-5'ax	1.143	H-4'ax, H-5'eq, H-6'eq, H-6'ax, H-4'eq	22.8
H-4'ax	0.720	H-4'eq, H-5'ax, H-3'a	26.5
H-5'eq	1.660	H-4'eq, H-6'eq, H-5'ax	22.8

[a] Chemical shifts relative to TMS (500 MHz ^{1}H spectrum). [b] Abbreviations: eq, equatorial; ax, axial.

Table 3

Chemical Shifts Differences Δδ Between Protons of 3 and 4

Δδ geminal	3	4
Δδ = δ H-4'eq - H-4'ax	0.63	0.91
Δδ = δ H-5'eq - H-5'ax	0.49	0.36
Δδ = δ H-6'eq - H-6'ax	-0.42	-0.25

Δδ of corresponding protons

Δδ = δ H-4'ax (**3**) - δ H-4'ax (**4**) = 0.80
Δδ = δ H-4'eq (**3**) - δ H-4'eq (**4**) = 0.52
Δδ = δ H-5'ax (**3**) - δ H-5'ax (**4**) = 0.03
Δδ = δ H-5'eq (**3**) - δ H-5'eq (**4**) = 0.16
Δδ = δ H-6'ax (**3**) - δ H-6'ax (**4**) = 0.26
Δδ = δ H-6'eq (**3**) - δ H-6'eq (**4**) = 0.19

anisotropy from the cyclohexane ring [7]. Herein, H-3' in **3** (pseudoaxial) is localized at a higher field (δ_H 5.157) than H-3' in **4** (pseudoequatorial δ_H 5.831) deshielded by the magnetic anisotropy from the C-3'a-C-4' bond. The H-3'a in **3** (δ_H = 3.218) is more shielded when it is *cis* than *trans* **4** to an aryl substitutent [8]. An unambiguous assignment of the H-3' and H-3'a spatial relationship was performed using a set of NOE experiments. The irradiation of H-3'a, on δ_H 3.650, leads to a strong NOE differential with H-3', H-4'eq and H-5'ax protons for product **4**. Consequently H3'a/H-3' are in a *cis* relationship. The broad singlet at δ_H 3.415 was assigned to the H-3 proton and the eight peak multiplet at δ_H 3.650 for the proton at C-3'a. The remaining six different multiplets for C-4', C-5' and C-6' methylene protons were unambiguously assigned by the use of a COSY experiment (Table 2). The unusual chemical shift observed for H-6'eq (δ_H 1.230) suggests that the latter suffers from shielding effects from the phenyl group on C-3', leaving the H-6'ax (δ_H 1.480) deshielded by the magnetic anisotropy from aziridine ring [9-10].

On the other hand, Johnson and Bovey [11] have described the downfield shift of these protons as a function of their distance from the aromatic ring. This particular correlation is useful when one is dealing with two isomers in which there is a variation in the spatial relationship of a distinctive proton and a phenyl group. As can be observed in Table 3, the chemical shift differences among the protons in **3** and **4**, in particular H-4'ax, H-4'eq, H-5'eq

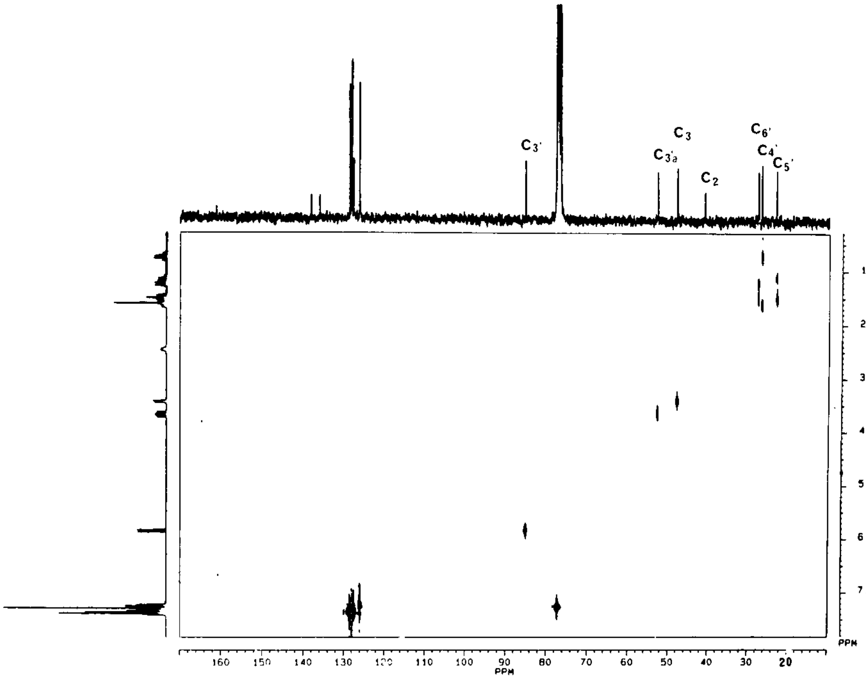

Figure 2. Heteronuclear correlation of 4.

and H-6'ax underwent diamagnetic shielding from the aromatic ring attached on C-3'. The ^{13}C signal assignments for compound **4** were confirmed by ^{1}J(CH) HETCOR experiments (Table 2 and Figure 2). Thus, C-5' at δ_C 22.8 was correlated with the proton signals at δ_H 1.500 (H-5'eq) and δ_H 1.143 (H-5'ax), and the C-4' carbon at δ_C 26.5 was correlated with the proton signals at δ_H 1.630 (H-4'eq) and δ_H 0.720 (H-4'ax). Finally, the C-6' methylene carbon at δ_C 27.4 correlated with protons H-6'eq at δ_H 1.230 and H-6'ax at δ_H 1.480. The doublet at δ_H 5.831 (H-3') was correlated with the carbon signal at δ_C 85.0 (C-3'), the C-3 signal at δ_C 47.7 correlated with H-3 proton at δ_H 3.415 and the signal at δ_H 3.650 (H-3'a) correlated with the C-3'a at δ_C 52.6. To confirm the coupling constant assignment, we have performed a Double Quantum Filtered COSY [12] determined at 500 MHz (Figure 3) and the magnitudes of coupling constants were tested by simulating the spectrum (Figure 4).

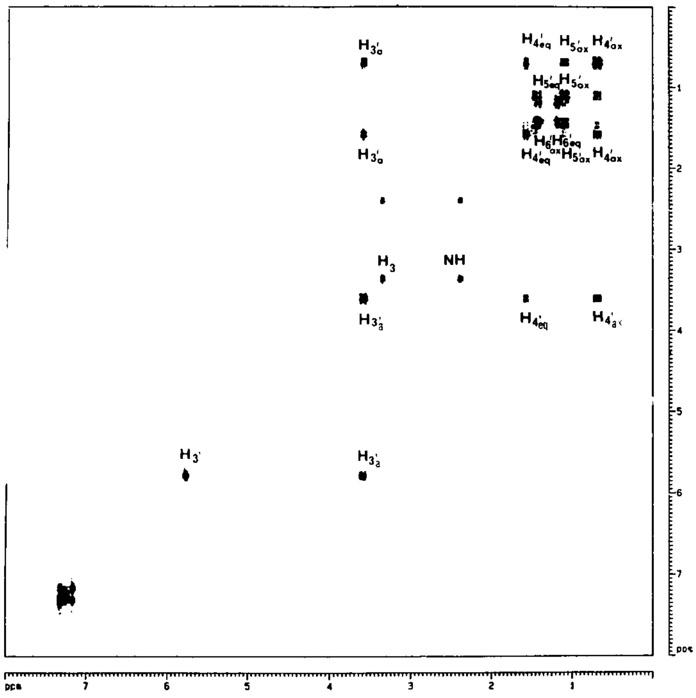

Figure 3. Double quantum filtered Cosy of **4**.

In order to verify the proposed structure and stereochemistry of **4**, a single-crystal X-ray data study was carried out (drawings of **3** and **4** are shown in Figure 5). The results confirmed the *syn* configuration of protons at C-3' and C-3'a as well as the α orientation of the aziridine ring proposed for **4**.

EXPERIMENTAL

The nmr spectra were obtained on a Varian VXR-300, XL-400 and Bruker 500AM spectrometers equipped with a 5-mm multinuclear probe. The spectra were recorded at room temperature on samples of *ca.* 20-mg in 0.5 ml of deuteriochloroform using TMS as the internal standard. Connectivities between protons were established by 2D correlated spectroscopy (COSY) using pulse sequence D$_1$-90°-D$_0$-45°-FID (2-3) SW$_2$ = 3289, SW$_1$ = 7644. COSY was obtained with 1024 t$_1$ values and, prior to Fourier transformation, the t$_2$ and t$_1$ domain FIDs were multiplied with a non shifted sine bell window function. The HETCOR conditions were as follows: all ^{13}C, ^{1}H and ^{13}C 2D nmr spectra were recorded on Bruker WM-300 spectrometer equipped with a 5 mm multinuclear probe (probe temperature 18°); the

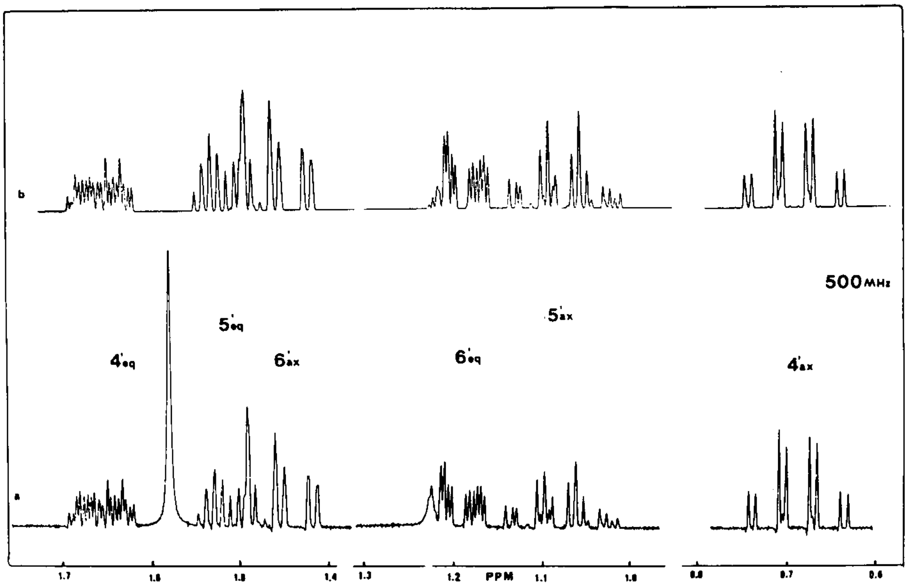

Figure 4. Observed and simulated 500-MHz ^{1}H nmr spectra of **4**.

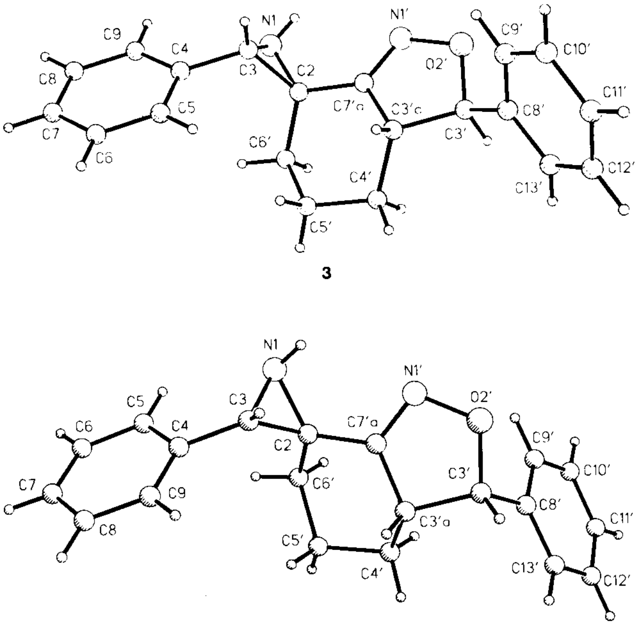

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Figure 5. Perspective drawings of 3 and 4 showing atom labeling.

spectra were obtained with an F_1 (^1H) spectra width of 1666 Hz with 128 time increments and zero-filled to 512; the F_2 (^{13}C) spectral width was 13888 Hz with 2048 data points 240 transients were collected for each time increment with a relaxation delay of 2 s. The double-quantum filtered COSY experiment was run on a Bruker AM-500 spectrometer. Phase-sensitive detection was obtained using the time proportional phase incrementation (TPPI) method. The parameters were: 2K x 529 complex points in the time domain transformed to 1K x 1K real points in the frequency domain; window function: sine bell shifted by π/5 in both dimensions; acquisition time: 0.1995; recycling time: 2 s; spectral width: 10.3 ppm (5150 Hz); number of accumulations: 48.

Table 4

Atom Coordinates (x10^4) and Temperature Factors (A^2 x 10^3) for Aziridine **3**

Atom	x	y	z	U
N(1)	10575(3)	1232(1)	5884(2)	66(1)*
C(2)	10226(3)	1511(1)	4405(3)	49(1)*
C(3)	9187(3)	1666(1)	5128(3)	52(1)*
C(4)	9160(3)	2373(1)	5815(3)	53(1)*
C(5)	8509(4)	2969(1)	4936(3)	60(1)*
C(6)	8507(4)	3613(1)	5574(3)	66(2)*
C(7)	9150(4)	3683(2)	7103(3)	70(2)*
C(8)	9775(4)	3097(2)	7985(3)	66(2)*
C(9)	9779(4)	2449(2)	7354(3)	63(1)*
N(1')	9447(3)	375(1)	3109(2)	60(1)*
O(2')	8767(2)	119(1)	1610(2)	65(1)*
C(3')	8863(4)	679(1)	645(3)	54(1)*
C(3')a	9048(3)	1353(1)	1557(2)	53(1)*
C(4')	10174(4)	1911(1)	1492(3)	64(2)*
C(5')	10628(4)	2431(1)	2775(3)	64(2)*
C(6')	11299(4)	2069(1)	4289(3)	61(1)*
C(7')a	9580(3)	1045(1)	3073(2)	50(1)*
C(8')	7481(5)	649(1)	-850(3)	48(2)*
C(9')	6003(6)	633(1)	-928(3)	62(2)*
C(10')	4702(4)	640(1)	-2308(3)	71(2)*
C(11')	4882(4)	657(1)	-3589(3)	75(2)*
C(12')	6346(6)	665(1)	-3524(3)	74(2)*
C(13')	7622(4)	658(1)	-2158(3)	63(2)*

*** Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i,j) tensor.**

Table 5

Bond Lengths (Å) for Aziridine **3**

N(1)-C(2)	1.457(3)	N(1)-C(3)	1.458(4)
C(2)-C(3)	1.488(5)	C(3)-C(4)	1.502(4)
C(4)-C(5)	1.392(4)	C(5)-C(6)	1.371(4)
C(6)-C(7)	1.375(4)	C(7)-C(8)	1.375(4)
C(4)-C(9)	1.387(4)	C(8)-C(9)	1.373(4)
N(1')-O(2')	1.426(2)	O(2')-C(3')	1.457(3)
C(3')-C(3')a	1.525(3)	C(3')a-C(4')	1.527(5)
C(4')-C(5')	1.514(4)	C(2)-C(6')	1.510(4)
C(5')-C(6')	1.516(4)	C(2)-C(7')a	1.481(3)
N(1')-C(7')a	1.272(3)	C(3')a-C(7')a	1.483(3)
C(3')-C(8')	1.498(3)	C(8')-C(9')	1.382(8)
C(9')-C(10')	1.393(4)	C(10')-C(11')	1.359(5)
C(11')-C(12')	1.374(7)	C(8')-C(13')	1.366(5)
C(12')-C(13')	1.373(4)		

Table 6

Bond Angles (°) in Aziridine **3**

C(2)-N(1)-C(3)	61.4(2)	N(1)-C(2)-C(3)	59.3(2)
N(1)-C(2)-C(6')	117.8(2)	C(3)-C(2)-C(6')	121.4(2)
N(1)-C(2)-C(7')a	120.7(2)	C(3)-C(2)-C(7')a	116.3(2)
C(6')-C(2)-C(7')a	112.1(3)	N(1)-C(3)-C(2)	59.3(2)
N(1)-C(3)-C(4)	117.1(2)	C(2)-C(3)-C(4)	122.9(3)
C(3)-C(4)-C(5)	121.4(2)	C(3)-C(4)-C(9)	120.7(2)
C(5)-C(4)-C(9)	117.9(2)	C(4)-C(5)-C(6)	121.0(3)
C(5)-C(6)-C(7)	120.4(3)	C(6)-C(7)-C(8)	119.2(3)
C(7)-C(8)-C(9)	120.7(3)	C(4)-C(9)-C(8)	120.8(2)
O(2')-N(1')-C(7')a	108.1(2)	N(1')-O(2')-C(3')	108.3(2)
O(2')-C(3')-C(3')a	103.6(2)	O(2')-C(3')-C(8')	110.1(2)
C(3')a-C(3')-C(8')	116.4(2)	C(3')-C(3')a-C(4')	116.7(3)
C(3')-C(3')a-C(7')a	100.3(2)	C(4')-C(3')a-C(7')a	112.2(2)
C(3')a-C(4')-C(5')	111.0(3)	C(4')-C(5')-C(6')	112.8(2)
C(2')-C(6')-C(5')	112.5(2)	C(2)-C(7')a-N(1')	124.9(2)
C(2)-C(7')a-C(3')a	120.1(2)	N(1')-C(7')a-C(3')a	115.0(2)
C(3')-C(8')-C(9')	119.6(3)	C(3')--C(8')-C(13')	122.2(4)
C(9')-C(8')-C(13')	118.1(3)	C(8')-C(9')-C(10')	120.4(4)
C(9')-C(10')-C(11')	120.0(4)	C(10')-C(11')-C(12')	120.0(3)
C(11')-C(12')-C(13')	119.6(4)	C(8')-C(13')-C(12')	121.8(4)

Spectral simulations were performed using the PANIC program of Bruker software. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer at 70 eV. The mixture of products **1-4** was prepared as reported earlier [3].

Separation of **1** and **4**.

A benzene solution of a mixture of **1** and **4** containing 6 equivalents of silver oxide was heated to reflux using an ultrasonic bath (Branson 2200) operated at 200 eV for 15 minutes. After cooling, the resulting mixture was filtered on Celite and the filtrate evaporated *in vacuo*. The residue was purified by preparative silica gel

Table 7

Anizotropic Temperature Factors (A^2 x 10^3) for Aziridine **3**

Atom	U11	U22	U33	U23	U13	U12
N(1)	85(2)	45(1)	55(1)	2(1)	19(1)	2(1)
C(2)	45(2)	45(1)	53(1)	2(1)	18(1)	0(1)
C(3)	39(2)	58(1)	58(1)	4(1)	21(1)	-0(1)
C(4)	49(2)	53(2)	60(1)	-5(1)	27(1)	-9(1)
C(5)	63(3)	58(2)	61(2)	-2(1)	30(1)	-0(1)
C(6)	68(3)	54(2)	87(2)	7(1)	45(2)	4(2)
C(7)	78(3)	59(2)	87(2)	-17(2)	49(2)	-13(2)
C(8)	71(3)	68(2)	62(2)	-13(1)	31(2)	-13(2)
C(9)	69(3)	58(2)	57(2)	-3(1)	24(1)	-8(1)
N(1')	75(2)	45(1)	49(1)	1(1)	16(1)	-1(1)
O(2')	87(2)	43(1)	51(1)	1(1)	17(1)	0(1)
C(3')	64(3)	48(2)	53(2)	1(1)	27(1)	6(1)
C(3')a	59(2)	41(1)	54(1)	3(1)	21(1)	5(1)
C(4')	73(3)	54(2)	71(2)	6(1)	37(2)	2(2)
C(5')	65(3)	51(2)	85(2)	-1(1)	42(2)	-11(1)
C(6')	57(2)	52(1)	73(2)	-8(1)	26(2)	-5(1)
C(7')a	50(2)	42(1)	54(1)	3(1)	20(1)	2(1)
C(8')	51(3)	43(1)	53(2)	-1(1)	25(2)	6(1)
C(9')	73(3)	60(2)	53(2)	-2(1)	27(2)	8(2)
C(10')	59(3)	67(2)	75(2)	-6(1)	19(2)	3(2)
C(11')	90(3)	56(2)	57(2)	-4(1)	10(2)	7(2)
(C12')	110(4)	58(2)	51(2)	3(1)	32(2)	3(2)
C(13')	76(3)	57(2)	57(2)	-1(1)	31(2)	2(1)

The anisotropic temperature factor exponent takes the form:
$-2pi(H^2a^{*2}U11+K^2b^{*2}U22+ \ldots +2HKa^*b^*U12)$.

Table 8

Hydrogen Coordinates (x10^3) and Temperature Factors (A^2 x 10^3) for Aziridine **3**

Atom	x	y	z	U
H(1)	1030(3)	83(2)	575(3)	6
H(3)	809(1)	162(1)	480(1)	6
H(5)	806(1)	293(1)	387(1)	6
H(6)	805(1)	402(1)	495(1)	6
H(7)	916(1)	414(1)	755(1)	6
H(8)	1021(1)	314(1)	905(1)	6
H(9)	1022(1)	205(1)	799(1)	6
H(3')	972(1)	64(1)	39(1)	6
H(3')a	811(1)	163(1)	119(1)	6
H(4')a	968(1)	216(1)	56(1)	6
H(4')b	1109(1)	168(1)	155(1)	6
H(5')a	1139(1)	275(1)	274(1)	6
H(5')b	972(1)	269(1)	266(1)	6
H(6')a	1149(1)	242(1)	505(1)	6
H(6')b	1226(1)	185(1)	445(1)	6
H(9')	587(1)	62(1)	-2(1)	6
H(10')	368(1)	63(1)	-235(1)	6
H(11')	399(1)	66(1)	-454(1)	6
H(12')	648(1)	67(1)	-443(1)	6
H(13')	864(1)	66(1)	-212(1)	6

Table 9

Crystal and Empirical Data for Aziridine **4**

Emperical Formula	C(20)H(20)N(2)O(1)
Formula Weight	304.39
Crystal System	Monoclinic
Lattice Parameters:	a = 11.134 (5) angstrom
	b = 6.435 (2) angstroms
	c = 23.696 (7) angstroms
	beta = 101.42 (3) degrees
	V = 1664 (2) angstroms^3
Space Group	$P2_1/c$ (#14)
Z value	4
Dcalcd	1.21 g cm^{-3}
F000	648
mu (CuK-alpha)	5.58 cm^{-1}
Diffractometer	NICO
Radiation	CuK-alpha (lambda = 1.54178) Ni-filtered
Temperature	23 degrees Cent.
2-theta (max)	110.1 degrees
No. Observations (I>3.00(sig(I)))	904
No. Variables	212
Residuals: R; Rw	0.057; 0.074
Goodness of Fit Indicator	1.47
Maximum Shift in Final Cycle	0.04
Largest Peak in Final Diff. Map	0.21 e angstrom^{-3}

Table 10

Intramolecular Bond Angles in Aziridine **4**

atom	atom	atom	angle	atom	atom	atom	angle
N1'	O2'	C3'	109.5(5)	H7	C7	C6	120.36
H1	N1	C2	102(5)	H7	C7	C8	119.20
H1	N1	C3	102(5)	C6	C7	C8	120.4(8)
C2	N1	C3	61.1(4)	H8	C8	C7	120.34
C7'A	N'1	O2'	107.1(6)	H8	C8	C9	119.69
N1	C2	C7'A	122.1(5)	C7	C8	C9	120.0(8)
N1	C2	C3	60.2(5)	H9	C9	C4	119.72
N1	C2	C6'	118.2(6)	H9	C9	C8	120.07
C7'A	C2	C3	118.7(5)	C4	C9	C8	120.2(7)
C7'A	C2	C6'	110.3(6)	H3'	C3'	02'	108.71
C3	C2	C6'	119.5(5)	H3'	C3'	C8'	108.41
H3	C3	N1	115.00	H3'	C3'	C3'A	108.62
H3	C3	C4	114.99	O2'	C3'	C8'	110.8(6)
H3	C3	C2	114.93	O2'	C3'	C3'A	104.3(6)
N1	C3	C4	117.4(6)	C8'	C3'	C3'A	115.7(6)
N1	C3	C2	58.7(4)	H3'A	C3'A	C7'A	108.90
C4	C3	C2	123.9.5	H3'A	C3'A	C3'	108.98
C9	C4	C5	119.8(6)	H3'A	C3'A	C4'	109.27
C9	C4	C3	118.7(7)	C7'A	C3'A	C3'	99.8(6)
C5	C4	C3	121.5(7)	C7'A	C3'A	C4'	111.3(6)
H5	C5	C4	120.50	C3'	C3'A	C4'	118.0(6)
H5	C5	C6	120.69	H4'A	C4'	H4'B	109.40
C4	C5	C6	118.8(7)	H4'A	C4'	C5'	109.50
H6	C6	C7	119.45	H4'A	C4'	C3'A	109.82
H6	C6	C5	119.82	H4'B	C4'	C5'	109.30
C7	C6	C5	120.7(8)	H4'B	C4'	C3'A	109.38

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 11

Positional Parameters for Aziridine 4

atom	x	y	z
O2'	0.3995(4)	-0.139(1)	0.1934(2)
N1	0.6630(6)	0.351(1)	0.1848(3)
N1'	0.4724(5)	0.043(1)	0.1928(2)
C2	0.6441(6)	0.155(1)	0.1528(3)
C3	0.7573(6)	0.185(1)	0.1982(2)
C4	0.8813(6)	0.230(1)	0.1855(2)
C5	0.9078(7)	0.419(1)	0.1626(3)
C6	1.0258(9)	0.453(1)	0.1528(3)
C7	1.1130(8)	0.308(2)	0.1665(4)
C8	1.0868(7)	0.121(2)	0.1890(3)
C9	0.9703(7)	0.082(1)	0.1984(3)
C3'	0.4255(6)	-0.284(1)	0.1513(4)
C3'A	0.5477(5)	-0.208(1)	0.1375(3)
C4'	0.5597(6)	-0.200(1)	0.0738(3)
C5'	0.6683(6)	-0.063(1)	0.0679(3)
C6'	0.6538(6)	0.157(1)	0.0895(2)
C7'A	0.5529(6)	0.000(1)	0.1627(3)
C8'	0.3191(7)	-0.298(2)	0.1005(3)
C9'	0.2432(8)	-0.136(1)	0.0850(3)
C10'	0.1483(7)	-0.147(2)	0.0372(4)
C11'	0.134(1)	-0.324(3)	0.0066(4)
C12'	0.207(1)	-0.492(2)	0.0203(6)
C13'	0.303(1)	-0.476(2)	0.0691(6)
H1	0.620(6)	0.33(1)	0.211(3)
H3	0.7578	0.1125	0.2329
H5	0.8467	0.5238	0.1539
H6	1.0446	0.5800	0.1362
H7	1.1937	0.3337	0.1609
H8	1.1483	0.0165	0.1978
H9	0.9521	-0.0469	0.2140
H3'	0.4379	-0.4177	0.1686
H3'A	0.6125	-0.2893	0.1586
H4'A	0.4869	-0.1454	0.0511
H4'B	0.5730	-0.3372	0.0610
H5'A	0.6741	-0.0570	0.0285
H5'B	0.7411	-0.1219	0.0897
H6'A	0.5819	0.2172	0.0672
H6'B	0.7231	0.2371	0.0851
H9'	0.2544	-0.0105	0.1068
H10'	0.0945	-0.0334	0.0263
H11'	0.0689	-0.3330	-0.0261
H12'	0.1959	-0.6151	-0.0021
H13'	0.3564	-0.5901	0.0802

thin layer chromatography. The pure compound **4**, mp 115-116° was obtained with 0.5% yield; ms: m/z (relative intensity) 304 (M$^+$, 0.3), 198 (10), 197 (11), 95 (100).

Anal. Calcd. for $C_{20}H_{20}N_2O$ (MW 304.38): C, 78.92; H, 6.62; N, 9.20. Found: C, 78.68; H, 6.52; N, 9.38.

X-ray Analysis.

X-ray determination of **4** was carried out on samples recrystallized from a chloroform-diisopropyl ether mixture, monoclinic, space group $P2_1/n$, a = 11.134(5) Å, b = 6.435(2) Å, c = 23.696(7) Å, β = 101.42(3)°, V = 1664(2) Å^3, Z = 4, λ = 1.54178 Å (CuKα), ρ_{calc} = 1.25 g cm^{-3}. Intensities were collected on a Nicolet R3m diffractometer using Ni-filtered CuKα

Table 11

Intramolecular Bond Angles in Aziridine 4

atom	atom	atom	angle	atom	atom	atom	angle
C5'	C4'	C3'A	109.4(5)	C9'	C8'	C3'	121.4(8)
H5'B	C5'	H5'A	109.37	C13'	C8'	C3'	119(1)
H5'B	C5'	C6'	109.03	H9'	C9'	C8'	119.99
H5'B	C5'	C4'	108.83	H9'	C9'	C10'	119.05
H5'A	C5'	C6'	109.11	C8'	C9'	C10'	121.0(8)
H5'A	C5'	C4'	108.78	H10'	C10'	C11'	120.35
C6'	C5'	C4'	111.7(5)	H10'	C10'	C9'	121.08
H6'A	C6'	H6'B	109.37	C11'	C10'	C9'	118.6(9)
H6'A	C6'	C5'	109.08	H11'	C11'	C10'	118.81
H6'A	C6'	C2	109.36	H11'	C11'	C12'	118.39
H6'B	C6'	C5'	109.00	C10'	C11'	C12'	123(1)
H6'B	C6'	C2	109.19	H12'	C12'	C11'	121.54
C5'	C6'	C2	110.8(6)	H12'	C12'	C13'	120.87
N1'	C7'A	C3'A	116.6(7)	C11'	C12'	C13'	118(1)
N1'	C7'A	C2	121.6(8)	H13'	C13'	C8'	119.73
C3'A	C7'A	C2	121.8(6)	H13'	C13'	C12'	120.01
C9'	C8'	C13'	119.8(8)	C8'	C13'	C12'	120(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 12

Intramolecular Distances (Å) in Aziridine 4

atom	atom	distance	atom	atom	distance
O2'	N1'	1.424(7)	C3'	C3'A	1.541(8)
O2'	C3'	1.440(8)	C3'A	H3'A	0.948
N1	H1	0.87(6)	C3'A	C7'A	1.47(1)
N1	C2	1.463(8)	C3'A	C4'	1.541(8)
N1	C3	1.487(8)	C4'	H4'A	0.948
N1'	C7'A	1.281(7)	C4'	H4'B	0.953
C2	C7'A	1.474(9)	C4'	C5'	1.528(9)
C2	C3	1.500(8)	C5'	H5'B	0.950
C2	C6'	1.525(8)	C5'	H5'A	0.951
C3	H3	0.945	C5'	C6'	1.521(9)
C3	C4	1.498(9)	C6'	H6'A	0.950
C4	C9	1.362(8)	C6'	H6'B	0.951
C4	C5	1.391(9)	C8'	C9'	1.347(9)
C5	H5	0.950	C8'	C13'	1.36(1)
C5	C6	1.40(1)	C9'	H9'	0.952
C6	H6	0.947	C9'	C10'	1.39(1)
C6	C7	1.34(1)	C10'	H10'	0.951
C7	H7	0.949	C10'	C11'	1.34(1)
C7	C8	1.37(1)	C11'	H11'	0.950
C8	H8	0.952	C11'	C12'	1.35(1)
C8	C9	1.381(9)	C12'	H12'	0.950
C9	H9	0.948	C12'	C13'	1.41(1)
C3'	H3'	0.950	C13'	H13'	0.948
C3'	C8'	1.51(1)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

radiation. The crystal structure was solved by direct methods and refined by full-matrix least-squares using SHELXTL program package [13] on DEC VAXSTATION II computer. (For details, see Tables 9-12).

X-ray determination of **3** was carried out on a sample crystallized from chloroform-diisopropyl ether, crystal size 0.20 x 0.24 x 0.36 mm, monoclinic, space group $P2_1/n$, a = 9.567(2) Å, b = 18.849(5) Å, c = 9.948(3) Å, β = 115.92(2)°, V = 1613.3 $Å^3$, Z = 4, λ = 1.54178 Å (CuKα), ρ_{calc} = 1.25 g cm^{-3} (For details, see Tables 4-8).

REFERENCES AND NOTES

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[1] A. Quilico, The Chemistry of Heterocyclic Compounds, Vol **17**, R. H. Wiley, ed, Interscience, New York, London, 1962, p 95.

[2] J. L. Aguilera, G. Sosa, W. F. Reynolds, E. Díaz and H. Barrios, *Magn. Reson. Chem.*, **27**, 823 (1989).

[3] E. Díaz, H. Barrios, B. Ortiz, R. Sánchez-Obregón, F. Yuste, W. F. Reynolds, J. L. Aguilera and E. Caballero, *Magn. Reson. Chem.*, **27**, 719 (1989).

[4a] G. Bodenhausen and R. Freeman, *J. Magn. Reson.*, **28**, 471 (1978); [b] A. Bax and S. K. Sakar, *J. Magn. Reson.*, **60**, 170 (1984).

[5] W. F. Reynolds, D. W. Hughes, M. Perpick-Dumont and R. G. Enriquez, *J. Magn. Reson.*, **63**, 413 (1985).

[6a] M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963); [b] H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

[7] R. A. Y. Jones, Annual Review of NMR Spectroscopy, Vol **1**, E. F. Mooney, ed, Academic Press, New York, 1968, p 8.

[8] A. Zysman, G. Dana and J. Wiemann, *Bull. Soc. Chim. France*, 1019 (1967).

[9] K. Tori, K. Aono, K. Kitahonoki, R. Muneyuki, Y. Takano, H. Tanida and T. Tsuji, *Tetrahedron Letters*, 2921 (1966).

[10] P. Mison, R. Chaaboumi, Y. Diab, A. Laurent, R. Martino, A. Lopez, F. Wehrli and T. Wirthlin, *Org. Magn. Reson.*, **8**, 90 (1976).

[11] C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[12a] D. Marion and K. Wüthrich, *Biochem. Biophys. Res. Commun.*, **113**, 967 (1983); [b] M. Rance, O. W. Sørensen, G. Bodenhausen, G. Wagner, R. R. Ernst and K. Wüthrich, *Biochem. Biophys. Res. Commun.*, **117**, 458 (1983); [c] G. E. Martin and A. S. Zektzer, Two Dimensional NMR Methods for Establishing Molecular Connectivity, VCH, New York, 1988, p 99.

[13] TEXSAN-TEXRAY, Structure Determination Package, Molecular Structure Determination, 1985.