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Asymmetric Nitrogen. 72. Geminal Systems. 46. *N*-Chlorooxaziridines: Optical Activation, Absolute Configuration, and Chiroptical Properties[1]

G. V. Shustov, S. V. Varlamov, I. I. Chervin, A. E. Aliev, R. G. Kostyanovsky,* D. Kim,[2] and A. Rauk*,[2]

Contribution from the Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R., and the Department of Chemistry, The University of Calgary, Calgary, Canada T2N 1N4. *Received October 5, 1988*

Abstract: The chiroptical properties of *N*-chlorooxaziridines are reported as derived experimentally and by means of ab initio quantum mechanical calculations. The synthesis and optical resolution of 2-chloro-1-oxa-2-azaspiro[2.5]octane (**1**) and the diastereomeric 2-chloro-5-methyl-1-oxa-2-azaspiro[2.5]octanes (**2a,b**) are described. The absolute configurations were determined by experimental spectroscopic techniques to be (+)-(2*R*)-**1**, (2*R*,3*S*,5*S*)-**2a**, and (2*S*,3*S*,5*S*)-**2b**. The assignments of absolute configuration at the N atom were confirmed by ab initio perturbative CI calculations on the parent compound (2*S*)-*N*-chlorooxaziridine (2*S*)-**3**. The first two electronic transitions of (2*S*)-**3** correspond to excitation of an electron from the highest occupied and second highest occupied molecular orbitals, respectively, to an antibonding molecular orbital localized to the N–Cl bond in each case. These transitions are calculated to have positive rotatory strength, in agreement with the observed CD spectra of (2*R*)-**1**, (2*R*,3*S*,5*S*)-**2a**, and (5*S*,3*S*,5*S*)-**2b**, after taking into consideration the opposite configurations at N of the first two compounds.

Earlier we have investigated the chiroptical properties of *N*-halogen-substituted aziridines and diaziridines as stereochemically rigid models of the *N*-halogenamine chromophore.[3] Stable *N*-chlorooxaziridines have recently been synthesized by us.[1,4] These compounds represent a new type of configurationally stable *N*-halogenamine chromophore containing an additional heteroatomic ligand, an oxygen atom. Typically, *N*-chlorooxaziridines have a barrier to inversion at nitrogen of 31.5 kcal mol^{-1} at 100 °C.[5] They have a characteristic long-wavelength UV absorption near 250 nm.[1,4] There have been no previous experimental or theoretical studies of the electronic structures or chiroptical properties of compounds containing this chromophore. Therefore, it is of interest to obtain *N*-chlorooxaziridines in optically active form[5] and to study their chiroptical properties. 2-Chloro-3,3-pentamethyleneoxaziridine (**1**) and its 5-methyl derivative **2** were prepared experimentally in optically active form and the absolute configurations established as described below. The parent compound, **3**, was investigated theoretically as a model for **1** and **2**.

Theoretical Method

The geometry of **3** was fully optimized by Hartree–Fock SCF calculations at the 6-31G* level[6] by using the GAUSSIAN 82 system of programs.[7] For the purpose of determining the transition properties, the wave functions were redetermined in center-of-mass coordinates and a modified basis set. For C, N, O, and H, the 6-31G basis set was used, augmented by the addition of a single diffuse s function and a set of diffuse p functions to N and O: $\alpha_N = 0.028$, $\alpha_O = 0.032$. Diffuse functions were not added to C or H. For the chlorine atom, the 12s,9p atom optimized basis set of Veillard[8] was contracted to 7s,5p by a Raffenetti-type contraction scheme.[9] A single set of 3d functions was added, as well as a single diffuse s function ($\alpha = 0.026$) and a set of diffuse p functions ($\alpha = 0.016$). The normal 3d polarization functions for C, N, O, and Cl had to be abandoned for reasons of economy. Addition of the diffuse functions is required to describe the lowest few Rydberg states. This basis set is referred to in the tables as the "diffuse" basis to distinguish it from the standard 6-31G* basis set.

A brief description of the theoretical method for the determination of oscillator and optical rotatory strengths is given below. A detailed account has been presented elsewhere.[10] Partially correlated wave functions for the ground and excited states are determined to first order in Rayleigh–Schrodinger perturbation theory. Thus

$$\Psi_n = \Psi_n{}^\circ - \textstyle\sum_j a_{nj}\Phi_j{}^\circ \qquad (1)$$

where

$$a_{nj} = \langle \Psi_n{}^\circ|\mathcal{H}|\Phi_j{}^\circ\rangle / (\langle \Phi_j{}^\circ|\mathcal{H}|\Phi_j{}^\circ\rangle - \langle \Psi_n{}^\circ|\mathcal{H}|\Psi_n{}^\circ\rangle) \qquad (2)$$

$\mathcal{H}$ is the exact Hamiltonian, $\Phi_j{}^\circ$ is a singlet singly or more highly excited configuration derived from the Hartree–Fock determinant Φ_{HF}, and $\Psi_n{}^\circ$ is a linear combination of quasidegenerate $\Phi_l{}^\circ$ ($l \neq j$) selected from at most singly excited configurations. Thus for the ground state, $\Psi_o{}^\circ = \Phi_{HF}$. All configurations for which the coefficient a_{nj} (eq 2) was greater than 0.03 were included in the zero-order part of the CI wave function.

Electric dipole transition moments in the length $\langle r\rangle_{on}$ and velocity $\langle v\rangle_{on}$ formalism and magnetic dipole transition moments $\langle m\rangle_{on}$ are explicitly evaluated from

$$\langle r\rangle_{on} = \langle \Psi_o|\mu|\Psi_n\rangle \qquad (3)$$

$$\langle v\rangle_{on} = \langle \Psi_o|\nabla|\Psi_n\rangle/(E_n - E_o) \qquad (4)$$

$$\langle m\rangle_{no} = -i\langle \Psi_n|\mathbf{m}|\Psi_o\rangle \qquad (5)$$

where the operators μ, ∇, and $\mathbf{m}$ have their usual definitions[10] and

$$E_n = \langle \Psi_n|\mathcal{H}|\Psi_n\rangle \qquad (6)$$

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(1) Previous paper in this series: Varlamov, S. V.; Shustov, G. V.; Shibaev, A. Yu.; Puzanov, Yu. V.; Chervin, I. I.; Kostyanovsky, R. G. *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.

(2) Department of Chemistry, University of Calgary, Calgary, Canada T2N 1N4.

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Oscillator strengths f_{on} are calculated by the "mixed" formalism

$$f_{on} = (2/3)\langle \Psi_o | \nabla | \Psi_n \rangle \cdot \langle r \rangle_{no} \qquad (7)$$

Optical rotatory strengths are evaluated as

$$[R_{no}]^r = \langle r \rangle_{on} \cdot \langle m \rangle_{no} \qquad (8)$$

and in the origin-independent form

$$[R_{on}]^v = \langle v \rangle_{on} \cdot \langle m \rangle_{no} \qquad (9)$$

The extent of deviation of $\langle r \rangle$ and $\langle v \rangle$ from collinearity and in magnitude is a measure of the quality of the wave functions and origin dependence of $[R]^r$.

Experimental Section

The NMR spectra were measured on a Bruker WM-400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz from TMS), the CD spectra on a Jasco J-500A spectropolarimeter with a DP-500N data processor, the UV spectra on a Specord UV–vis spectrophotometer, and optical rotation angles on a Polamat A polarimeter.

N-H-Oxaziridines (5*R*,*S*)-**4** and (5*S*)-**4** were obtained in the form of ethereal solutions from racemic and optically active (3*S*)-3-methylcyclohexanone **5** [$[\alpha]^{20}_D - 13.0°$ (neat)], respectively, as previously described.[11] Yields were in the range 25–30% as determined by iodometric titration. For the synthesis of [^{15}N]-(5R,S)-**4** and [^{15}N]-**6a**, hyroxylamine-*O*-sulfonic acid of 93% purity with 96.5% enrichment of ^{15}N was used. The ^{15}N content of ammonia for the synthesis of diazirine **6b** was 95.2%. The synthesis of *N*-H-oxaziridine **7** and racemic *N*-chlorooxaziridine **1** has been described.[1]

(−)-2-Chloro-1-oxa-2-azaspiro[2.5]octane (1). A solution of *N*-H-oxaziridine **7** (10.5 mmol) and *N*-chlorocamphorimide, $[\alpha]^{20}_D$ +6.0° (*c* 5.4, $CHCl_3$) (1 g, 4.6 mmol) in Et_2O (50 mL) was kept for 20 days at 20 °C (until the disappearance of **7** according to TLC), and the solvent was evaporated in vacuo. The products were extracted from the residue with pentane and, after removal of pentane, were separated by chromatography on silica (eluent, benzene). There was obtained *N*-chlorooxaziridine (−)-**1** (0.15 g, 22%; Table I) and *N*-chlorocyclohexanonimine.[1]

(5*R*,*S*)-2-Chloro-5-methyl-1-oxa-2-azaspiro[2.5]octane [(5*R*,*S*)-2]. A solution of *t*-BuOCl (1.4 g, 13 mmol) in Et_2O (30 mL) was added dropwise to *N*-H-oxaziridine (5*R*,*S*)-**4** (12.6 mmol) in Et_2O (100 mL) with cooling (−70 °C) and stirring. After 3 h at 20 °C the reaction mixture was washed with an aqueous solution of NH_2OSO_3H (0.2 g mL^{-1}) and twice with water, and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was distilled. *N*-Chlorooxaziridine (5*R*,*S*)-**2** (1.6 g, 79%), bp 63–64 °C (4 mm), was obtained. Found: C, 52.1; H, 7.4; N, 8.9. $C_7H_{12}ClNO$ requires: C, 52.0; H, 7.5; N, 8.7.

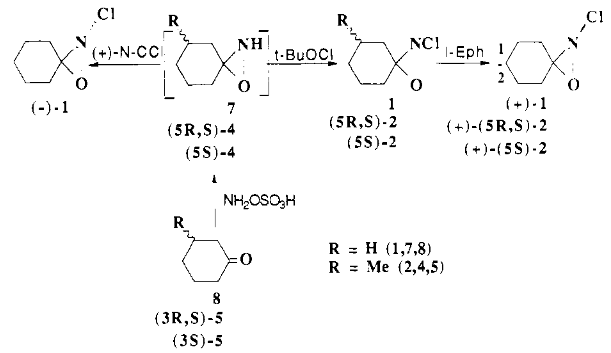
The same procedure was used to obtain [^{15}N]chlorooxaziridine (5*R*,*S*)-**2** from *N*-H-[^{15}N]oxaziridine (5*R*,*S*)-**4**.

(5*S*)-2-Chloro-5-methyl-1-oxa-2-azaspiro[2.5]octane [(5*S*)-2]. A solution of *t*-BuOCl (0.45 g, 4 mmol) in Et_2O (20 mL) was added dropwise to *N*-H-oxaziridine (5*S*)-**4** (3.9 mmol) in Et_2O (30 mL) with cooling (−70 °C) and stirring. After 3 h at 20 °C the solvent was evaporated in vacuo and the residue was chromatographed on silica. There was obtained *N*-chlorooxaziridine (5*S*)-**2** (0.43 g, 68%; Table I) (eluent, benzene) and initial ketone (3*S*)-**5** (0.56 g) (eluent, Et_2O).

Kinetic Resolution of *N*-Chlorooxaziridines 1 and 2 (General Procedure). A solution of l-ephedrine (0.5 g, 3 mmol) in Et_2O (10 mL) was added to *N*-chlorooxaziridine (3 mmol) in Et_2O (20 mL) with cooling (−20 °C) and stirring. The reaction mixture was kept for 7 days at 0 °C and for 3 days at 20 °C. The precipitate formed (l-ephedrine hydrochloride) was filtered off and the solution was evaporated in vacuo. The enriched *N*-chlorooxaziridine was extracted from the residue with pentane and, after removal of pentane, was purified by chromatography on silica (eluent, benzene), yield ~80% (Table I).

5-Methyl-1,2-diazaspiro[2.5]oct-1-ene (6). A solution, cooled to 0 °C, of NH_2OSO_3H (0.6 g, 4.9 mmol) in absolute MeOH (5 mL) was added dropwise to a solution of ketone (3*R*,*S*)-**5** (0.45 g, 4 mmol) in absolute MeOH, saturated with dry NH_3 at 0 °C and 1 h at 20 °C; the precipitated salt $(NH_4)_2SO_4$ was filtered off. The solution was evaporated in vacuo and the residue containing crude diaziridine (0.31 g, 62%) was dissolved in boiling ether (30 mL). To the resulting solution, cooled to 0 °C, was added a solution of NaOCl (2.7 mmol) in 4 mL of water dropwise with stirring. After separation of the organic layer, the aqueous solution was extracted with ether (2 × 5 mL), and the combined ethereal solution was successively washed by 10 mL of water, 10 mL of 10% aqueous NH_2OSO_3H (for removal of ketone), and 10 mL of water, and was dried ($CaCl_2$). After the solvent removal the residue was distilled in vacuo, providing diazirine **6** (0.12 g, 24%), bp 45 °C (30 mm). Found: C, 67.7; H, 9.7; N, 23.05. $C_7H_{12}N_2$ requires: C, 67.7; H, 9.7; N, 22.6.

Scheme I



By the same procedure there were obtained ^{15}N-labeled diazirines **6a** (yield 29%) and **6b** (yield 18%).

Results and Discussion

Experimental. The general method of obtaining optically active oxaziridines by an asymmetric oxidation of imines[12] is, apparently, unsuitable in the case of *N*-chlorooxaziridines, since we have found that at the oxidation of *N*-chlorocyclohexanonimine, the desired product, 2-chloro-3,3-pentamethyleneoxaziridine (**1**) is obtainable only in very low yield.[1] Alternatively, **1** can obtained with relatively low optical activity (Table I) by the chlorination of the *N*-H-oxaziridine **7** with a chiral chlorinating reagent, (+)-*N*-chlorocamphorimide (N-CCl). More effective has proved to be kinetic resolution at the action of l-(−)ephedrine (l-Eph) (Scheme I).

N-Chlorooxaziridine (+)-**1** is endowed with a marked optical activity (Table I) that cannot be due to optically active impurities, since it completely disappears upon addition of Et_3N producing the decomposition of *N*-chlorooxaziridine (+)-**1** to cyclohexanone **8**.[1,5]

To determine the absolute configuration of *N*-chlorooxaziridine (+)-**1** there were synthesized its derivatives (5*R*,*S*)-**2** and (5*S*)-**2**, which contain an additional chiral center C_5. From the ^1H and ^{13}C NMR spectra, both in the case of (5*R*,*S*)-**2** and (5*S*)-**2** there were observed only two sets of diastereomeric signals with an intensity ratio 1:1. Assignment of the signals (Tables II and III) was made on the basis of a joint analysis of the correlational 2D COSY spectra [(^1H, ^1H) and (^1H, ^{13}C)]. After the kinetic resolution with l-ephedrine, the ratio of diastereomers of *N*-chlorooxaziridine (5*R*,*S*)-**2** continued to be 1:1, while in the case of (5*S*)-**2** it changed to 1.5:1 (Table I).

A good agreement of the observed chemical shifts of the C_4 and C_8 nuclei in the ^{13}C spectra of diastereomers **2** with those calculated by the additive scheme on the basis of the ^{13}C chemical shifts of *N*-chlorooxaziridine[13] **1** by taking account of the deshielding effects[14] of the equatorial methyl group[15] at C_5 enables us to assume that the diastereomers differ in the mutual orientation of the 5-Me group and Cl atom. Furthermore, diastereomer **2a**, which was predominant in the mixture after the kinetic resolution of *N*-chlorooxaziridine (5*S*)-**2**, has a cis orientation, whereas the minor **2b** has a trans orientation. This is confirmed by the analysis of the coupling constants $^2J(^{13}C, ^{15}N)$ observed from the spectrum of [^{15}N]chlorooxaziridine (5*R*,*S*)-**2**.[17] Earlier, on the example of *N*-chloro-substituted aziridines **9a**,**b**[16] and diaziridines **10a**,**b**[18]

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(13) Assignment of the ^{13}C signals of C_4 and C_8 nuclei cis and trans oriented with respect to the Cl atom of *N*-chlorooxaziridine **1** was made on the basis of the known shielding effect of the N substituent; cf.: Jordan, G. J.; Crist, L. R. *Org. Magn. Reson.* **1977**, *9*, 322–324, as well as ref 1 and 17.

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(15) The equatorial orientation of the 5-Me group is confirmed by the magnitude of the constant ^3J of the proton 5-H_a with 4-H_a (Table II).

(16) Obtained by the reaction of racemic 3-methylcyclohexanone (3*R*,*S*)-**5** with $^{15}NH_2OSO_3H$ and a subsequent treatment with *t*-BuOCl.

Table I. Optical and Chiroptical Properties of *N*-Chlorooxaziridines **1** and **2** (in Heptane)

compd	$[\alpha]^{20}_D$, deg (*c*, vol %)	CD λ_{max}, nm ($\Delta\epsilon$)/[*R*][a]	UV λ_{max}, nm (ϵ)/*f*[a]
(−)-**1**	−1.0 (8.5)		
(+)-**1**	+14.6 (10.4)	235 (−0.271), 195 (+0.271)	253 (940), 205 (950)
		Gaussian components:[b]	Gaussian components:
		252.1 (−0.179)/−0.61/, 226.4 (−0.222)/−0.78/, 205 (+0.104)/+0.18/	252.2 (938)/0.0253/, 225.7 (380)/0.0050/, 204.4 (957)/0.0363/
(+)-(5*R*,*S*)-**2**	+15.9 (17.6)	253 (−0.412), 197 (+0.444)	253 (1080), 202 (1300)
(5*S*)-**2**[c]	+0.8 (7.2)	230 (−0.088)	
(+)-(5*S*)-**2**[d]	+21.9 (6.3)	235 (−0.444)	
(2*R*,3*S*,5*S*)-**2a**[e]		235 (−1.72)	
(2*S*,3*S*,5*S*)-^{2}b[e]		235 (+1.53)	

[a] For Gaussian components only; [*R*] ~ 1.08 × 10^{40} × *R* in CGSE; *f* in CGSE. [b] For sample (+)-**1** with $\Delta\epsilon_{235}$ − 0.253. [c] Ratio of diastereometers **2a**/**2b**, 50:50. [d] After the kinetic resolution, ratio of **2a**/**2b**, 61:39. [e] The CD spectra were obtained on DP-500N by solution of the system of equations, $\Delta\epsilon_1 = 0.50\Delta\epsilon_a + 0.50\Delta\epsilon_b$ and $\Delta\epsilon_2 = 0.61\Delta\epsilon_a + 0.39\Delta\epsilon_b$, where $\Delta\epsilon_1$ is the dichroic absorption of (5*S*)-**2** with the ratio of **2a**/**2b** of 50:50 and $\Delta\epsilon_2$ is the dichroic absorption of (+)-(5*S*)-**2** with the ratio of **2a**/**2b** of 61:39.

Table II. Chemical Shifts (δ) and Coupling Constants $^1J(^1H, ^{13}C)$ of *N*-Chlorooxaziridines and of Diazirine **6** in $CDCl_3$

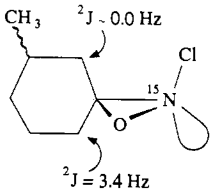
	3	4	5	6	7	8	Me
			$^{13}C(^1J_{CH}$, Hz)				
1[a]	86.45	33.56	24.42	23.92	30.10	24.42	
		(131.8)	(127.7)	(129.0)	(130.4)	(127.7)	
2a obsd	86.52	37.94	31.92	33.13	22.51	32.81	22.15
		(127.6)	(127.6)	(126.2)	(126.2)	(126.2)	(124.8)
2a calcd	86.50	39.13	30.32	32.95	24.47	33.78	
2b obsd	86.52	41.18	30.26	32.91	23.65	29.61	21.57
		(127.6)	(127.6)	(126.2)	(126.2)	(130.9)	(124.8)
2b calcd	86.5	42.59	30.32	32.95	24.47	30.32	
6	28.02	39.80	30.96	33.64	23.49	30.90	21.73
		(126.7)	(126.3)	(125.0)	(128.9)	(127.7)	(125.0)
			^1H				
2a (ax.)		1.68	1.72	0.95	1.45	1.78	0.97
2a (eq)		2.00		1.71	1.76	1.17	
2b (ax.)		1.51	1.68	0.98	1.54	1.93	0.89
2b (eq)		1.23		1.70	1.95	1.97	
6 (ax.)		1.42	1.82	1.06	1.61	1.68	0.93
6 (eq)		0.57		1.81	1.79	0.53	

[a] Parameters of PMR spectrum of *N*-chlorooxaziridine **1**; see ref 1.

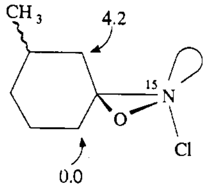
Table III. Coupling Constants (Hz) of *N*-Chlorooxaziridine **2** and Diazirine **6** in $CDCl_3$

constant	**2a**	**2b**	**6a**	**6b**
^2J(4a, 4e)		−13.3	−14.1	−14.1
^3J(4a, 5a)		11.7	11.3	11.3
^3J(4e, 5a)		3.7	3.9	3.9
^3J(5a, Me)	7.0	7.0	6.4	6.4
^2J(8a, 8e)	−14.1		−13.2	−13.2
^3J(8a, 7a)	12.7		11.7	11.7
^3J(8a, 7e)	4.5		4.5	4.5
^4J(8e, 4e)	2.0	2.0	1.8	1.8
^4J(8e, 6e)	2.0	2.0	1.8	1.8
^4J(4e, 6e)	2.0	2.0	1.8	1.8
$^3J(^{15}N$, 4e)		2.1	0.8	0.9
$^3J(^{15}N$, 4a)		0.0	0.0	1.1
$^3J(^{15}N$, 8e)	1.5		1.0	1.1
$^3J(^{15}N$, 8a)	0.0		0.0	1.1
$^1J(^{15}N, C_3)$	8.5	8.5	9.4	9.0
$^2J(^{15}N, C_4)$	0.0	4.2	1.2	1.5
$^2J(^{15}N, C_8)$	4.3	0.0	1.2	1.5
$^3J(^{15}N, C_5)$	0.0	1.7	0.0	0.0
$^3J(^{15}N, C_7)$	1.8	0.0	0.0	0.0

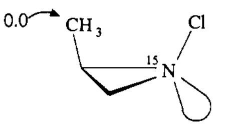
it was shown that the constants $^2J(^{13}C,^{15}N)$ have larger values for the ^{13}C nuclei cis oriented with respect to a lone pair of the ^{15}N atom. Correspondingly, in the ^{13}C spectrum of the major diastereomer **2a** with a cis orientation of the 5-Me group and Cl atom, there is observed the $^2J(^{13}C, ^{15}N)$ constant for the C_8 nucleus, while in the spectrum of the minor diastereomer **2b** with a trans orientation of 5-Me and Cl, the coupling to C_4 is observed.



2a



2b



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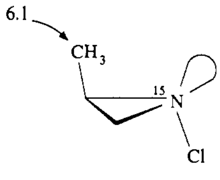

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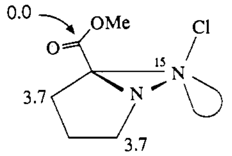
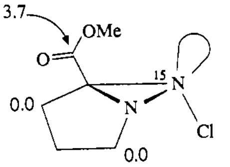


10a



10b

It is known that the values of the vicinal coupling constants ^3J are dependent on the dihedral angle between the respective nuclei and are, as a rule, close to zero for angles near 90°.

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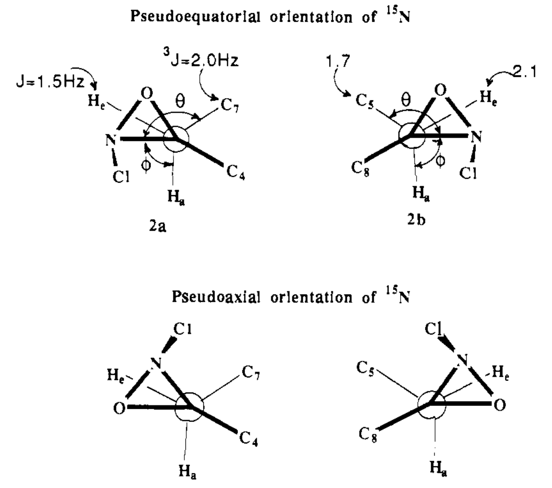
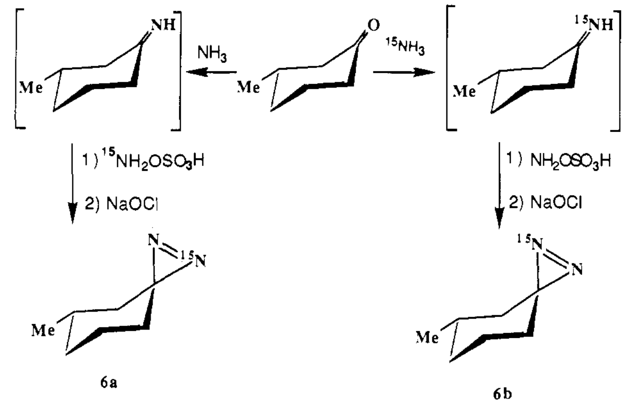
(18) Shustov, G. V.; Denisenko, S. N.; Chervin, I. I.; Zolotoi, A. B.; D'yachenko, O. A.; Konovalikhin, S. V.; Shilov, G. V.; Atovmyan, L. O.; Kostyanovsky, R. G. *Khim. Geterotsikl. Soedin.* **1986**, 1330–1333.

Chart I



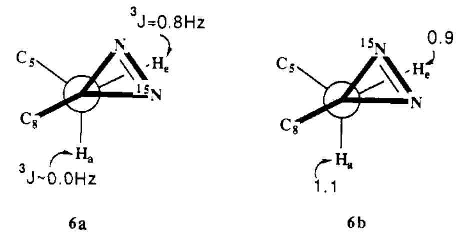
Scheme II



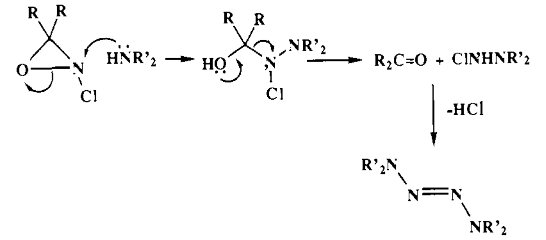
Therefore, the observed similar values of $^3J(^{13}C, ^{15}N)$ for the C_7 nucleus of the major diastereomer **2a** and at C_8 of the minor **2b** are an indication of similar values of the dihedral angle θ ($\sim 180°$). Moreover, one may presume a similar pseudoequatorial orientation of the N atom in diastereomers **2a,b**, since under an alternative pseudoaxial orientation the angles θ are close to 90°. A pseudoequatorial orientation of nitrogen is confirmed by similar values of $^3J(^1H, ^{15}N)$ for equatorial protons at C_4 of the major diastereomer **2a** and at C_8 of the minor **2b**. In the case of axial protons the angles ϕ are approximately 90°, and therefore the constants $^3J(^1H, ^{15}N)$ for them are absent (Chart I).

An additional confirmation of the pseudoequatorial orientation of the nitrogen in diastereomers of *N*-chlorooxaziridine **2** was obtained by studying model compounds—^{15}N-labeled diazirines **6a,b**. It is to be noted here that a similar pseudoequatorial position of the N atom and a different reciprocal orientation of the 5-Me group and Cl atom in the diastereomers **2a,b** presuppose a stereospecificity of the epimination of ketone **5** and a nonstereospecificity of the chlorination of *N*-H-oxaziridine **4**, which cannot be isolated because of its extreme instability. Such a stereochemistry of formation of diastereomers **2a,b** appears to be reasonable in the light of the known high stereoselectivity of nucleophilic addition to the C=O bond of 3-methylcyclohexanone[19] (**5**) and by taking into account the spatial remoteness of the 5-methyl group from the nitrogen atom in *N*-H-oxaziridine **4**, the latter being subject to attack from the chlorinating reagent. For bulky nucleophiles, to which we should refer anion $NH_2OSO_3^-$, there is a known preference for an equatorial attack on the C atom of the carbonyl group of ketone[19] **5**. A substitution of a NH group for the oxygen atom in this ketone will not, apparently, affect the stereochemistry of the epimination stage in the diazirine synthesis.

Chart II



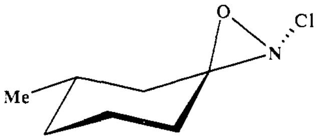
Scheme III



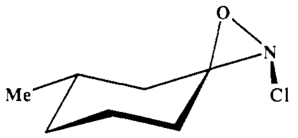
Therefore, we could expect a selective introduction of the label ^{15}N into a pseudoequatorial (**6a**) or pseudoaxial (**6b**) position of diazirine **6** and use this compound as a model for checking the validity of the conclusion about the orientation of the ^{15}N atom on the basis of the vicinal constants $^3J(^1H, ^{15}N)$,[20] (Scheme II).

Indeed, in the ^1H spectrum of isomer **6a** obtained with the use of $^{15}NH_2OSO_3H$, just as in the case of diastereomers of *N*-chlorooxaziridine **2**, there are observed the vicinal coupling constants $^3J(^1H, ^{15}N)$[21] for equatorial protons at C_4 and C_8, and their absence for the axial ones. Isomer **6b** has an alternate pseudoaxial orientation of the ^{15}N atom, and in its ^1H spectrum there are observed the constants $^3J(^1H, ^{15}N)$ for both the equatorial and axial protons at C_4 and C_8 (Chart II). Hence follows the validity of using the constants $^3J(^1H, ^{15}N)$ for a conformational analysis of substituted three-membered nitrogen heterocycles and, in particular, *N*-chlorooxaziridine **2**, as well as a preference for the equatorial attack of NH_2OSO_3H in the epimination of cyclohexanone derivatives.

On the basis of what has been said above we may conclude that diastereomer **2a**, prominant in the mixture after a kinetic resolution of *N*-chlorooxaziridine (5*S*)-**2**, has a (2*R*,3*S*,5*S*) absolute configuration and the minor **2b** has (2*S*,3*S*,5*S*).



2a



2b

Hence, the conservation of the equimolar ratio of diastereomers **2a,b** at the kinetic resolution of *N*-chlorooxaziridine (5*R*,*S*)-**2** is explained by the sensitivity of the reaction with the chiral amine to the configuration of the nitrogen chiral center alone. An extremely similar (practically enantiomeric) reactivity of diastereomers **2a,b** is manifested also in the reaction with achiral amines. Thus, at the action of shortage of morpholine on *N*-chlorooxaziridine (5*R*,*S*)-**2** the ratio of diastereomers continues to be 1:1. Such a stereochemistry of the reactions with amines appears to be due to a preference for the nucleophilic attack on the N atom of the oxaziridine ring[1] and spatial remoteness of the

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(19) Kamernitskii, A. V.; Akhrem, A. A. *Usp. Khim.* **1961**, *30*, 145–183.

(20) Diazirines **6a,b** are more convenient compared to the corresponding 1,2*H*-diaziridines for studying by the NMR technique, since in diazirines there are absent the effects [contributions into coupling constants ^2J and $^3J(^1H, ^{15}N$; $^{13}C, ^{15}N)$] associated with the orientation of the lone pair of the ^{15}N atom. Besides, in the ^1H spectra of diazirines **6a,b** the signals of protons at C_4 are not overlapped by those of other protons.

(21) In contrast to [^{15}N]chlorooxaziridines **2a,b**, for diazirines **6a,b** there are not observed vicinal constants $^3J(^{13}C, ^{15}N)$.

Table IV. Calculated Properties of (2*S*)-2-Chlorooxaziridine[a]

property			6-31G*	diffuse[a]
E_{SCF}, hartree			−627.671608	−627.59369
MO energies, eV	π^*_{ONCl}	20a	−11.65	−11.84[b]
	$3p_{Cl}$	19a	−12.46	−12.62[b]
	n_{ONCl}	18a	−13.32	−13.64
		17a	−14.78	−14.98
		16a	−15.58	−15.69
μ, D			2.942	3.262
$S_0 \rightarrow S_1$	*E*, eV			6.28
	$[R]^v$ ($[R]^r$)			+4.6 (+9.7)
	f			0.0282
	descriptn[c]			$\pi^*_{ONCl} \rightarrow \sigma^*_{NCl}$[b]
	$\langle r\rangle$, $\langle m\rangle$, $\langle v\rangle$[d]			0.374, 0.258, 0.528
	$\langle r\rangle\cdot\langle m\rangle$, $\langle v\rangle\cdot\langle m\rangle$, $\langle r\rangle\cdot\langle v\rangle$[e]			79, 74, 22
$S_0 \rightarrow S_2$	*E*, eV			7.00
	$[R]^v$ ($[R]^r$)			+4.1 (+2.5)
	f			0.0033
	descriptn[c]			$3p_{Cl} \rightarrow \sigma^*_{NCl}$[b]
	$\langle r\rangle$, $\langle m\rangle$, $\langle v\rangle$[d]			0.108, 0.542, 0.201
	$\langle r\rangle\cdot\langle m\rangle$, $\langle v\rangle\cdot\langle m\rangle$, $\langle r\rangle\cdot\langle v\rangle$[e]			74, 85, 30
$S_0 \rightarrow S_3$	*E*, eV			7.98
	$[R]^v$ ($[R]^r$)			+5.7 (−8.9)
	f			0.0122
	descriptn[c]			($0.53\pi^*_{ONCl} \rightarrow \sigma^*_{NO}$, $0.45n_{ONCl} \rightarrow \sigma^*_{NOCl}$)
	$\langle r\rangle$, $\langle m\rangle$, $\langle v\rangle$[d]			0.233, 0.581, 0.289
	$\langle r\rangle\cdot\langle m\rangle$, $\langle v\rangle\cdot\langle m\rangle$, $\langle r\rangle\cdot\langle v\rangle$[e]			80, 102, 22
$S_0 \rightarrow S_4$	*E*, eV			8.94
	$[R]^v$ ($[R]^r$)			−62.1 (−60.9)
	f			0.1163
	descriptn[c]			($0.41\pi^*_{ONCl} \rightarrow \sigma^*_{NO}$, $0.51n_{ONCl} \rightarrow \sigma^*_{NCl}$)
	$\langle r\rangle$, $\langle m\rangle$, $\langle v\rangle$[d]			0.719, 0.985, 0.738
	$\langle r\rangle\cdot\langle m\rangle$, $\langle v\rangle\cdot\langle m\rangle$, $\langle r\rangle\cdot\langle v\rangle$			110, 109, 1

[a] Geometry optimized with 6-31G* basis set (see Figure 3); see text for explanation of the diffuse basis set. [b] See Figure 4. [c] Each of the excitations terminates in an "excited" MO, which is a linear combination of canonical MOs. [d] Magnitudes in atomic units. [e] Angles in deg.

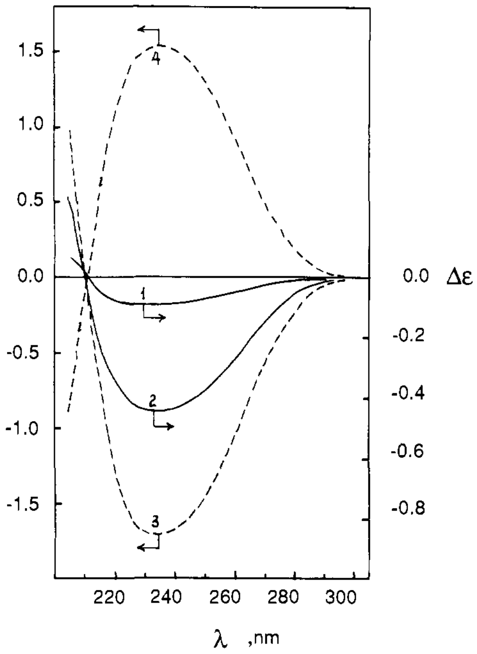


Figure 1. CD spectra of *N*-chlorooxaziridine (5*S*)-**2** before (1) and after (2) the kinetic resolution, and of the individual diastereomers (2*R*,3*S*,5*S*)-**2a** (3) and (2*S*,3*S*,5*S*)-**2b** (4) in heptane.

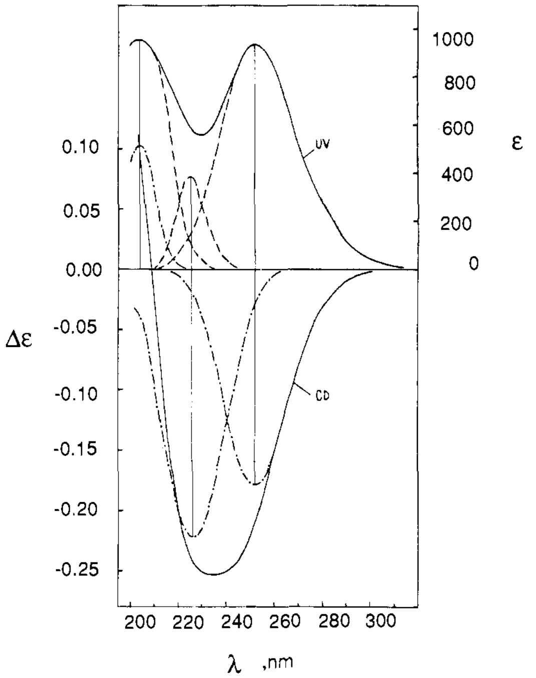


Figure 2. UV and CD spectra of *N*-chlorooxaziridine (+)-**1** in heptane and their Gaussian components: UV (---), CD (-·-).

chiral center C_5 (Scheme III).

From the CD spectra of *N*-chlorooxaziridine (5*S*)-**2** with a different known ratio of diastereomers **2a**,**b** there were obtained the spectra of individual diastereomers **2a** and **2b** (Table I, Figure 1). The similar values of the dichroic absorption of these diastereomers point to the fact that the sign of the Cotton effect (CE) of the long-wavelength band is principally determined by the absolute configuration of the nitrogen atom and is little dependent on the configuration of other chiral centers, C_3 and C_5. This is confirmed, moreover, by similar parameters of the CD spectra of enriched (+)-(5*R*,*S*)-**2**, (+)-(5*S*)-**2**, and *N*-chlorooxaziridine (+)-**1**, containing only a nitrogen chiral center (Table I). Hence, the absolute configuration of the latter can be assigned as (+)-(2*R*)-**1**. Comparison of the CE intensity at 235 nm of *N*-chlorooxaziridine (+)-**1** with an average intensity of the effects of diastereomers **2a**,**b** ($\Delta\epsilon$ ~1.63) enables us to estimate the optical purity of (+)-(2*R*)-**1**, ~17%.

For *N*-chlorooxaziridines (+)-**1** and (+)-**2** there is observed a significant difference in the form and position of UV and CD spectral bands (Table I, Figure 2). Decomposing these spectra

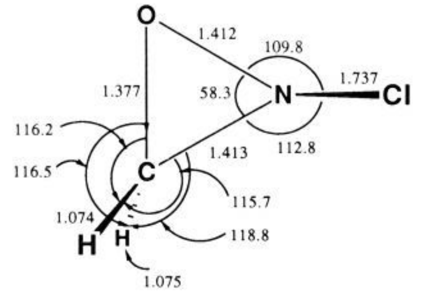
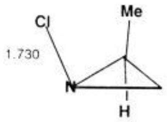


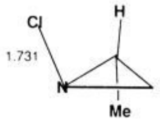
Figure 3. Geometry of (*S*)-**3** optimized at the 6-31G* level of theory: distances in Å, angles in degrees.

of *N*-chlorooxaziridine (+)-(2*R*)-**1** into the Gaussian components will indicate that a broad long-wavelength band at 235 nm in the CD spectrum is a superposition of, principally, two negative Cotton effects. This is in good agreement with the computational data described below, according to which the simplest (2*S*)-2-chlorooxaziridine (**3**) has two optically active transitions, close in energy, with positive rotational strength.

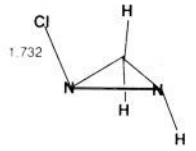
Theoretical. The 6-31G* optimized structure of (*S*)-*N*-chlorooxaziridine (2*S*)-**3** is shown in Figure 3. The N–Cl bond (1.737 Å) is intermediate in length to that previously found[3] for *N*-chloroaziridines **11** (cis Me, 1.730 Å; trans Me, 1.731 Å) and *trans*-*N*-chlorodiaziridine, *trans*-**12** (1.732 Å), and the longer N–Cl length of *cis*-**12** (1.746 Å), suggesting that the n_O–σ_{NCl}^* interaction is weaker than the n_N–σ_{NCl}^* interaction which is responsible for the longer bond of *cis*-**12**. Electronic excitation among these frontier orbitals of **3** will dominate the chiroptical properties of the lower excited states, as discussed below.



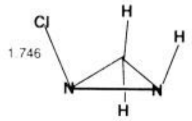
cis-11



trans-11



trans-12



cis-12

The three highest occupied molecular orbitals of **3** are shown in Figure 4. These MOs are involved in the electronic transitions discussed. The HOMO is an antibonding combination of nonbonding orbitals from each of the heteroatoms and is designated π^*_{ONCl}. The second highest occupied MO is highly localized to the Cl atom and is designated $3p_{Cl}$. The third highest occupied MO consists of the same nonbonding local orbitals as the HOMO but with a greater component from the oxygen atom, and is denoted as n_{ONCl}.

The lowest electronically excited state originates from excitation from the HOMO. The next two states are found by the CI method to arise by excitation from mixtures of the π^* and n MOs. The distribution of the "excited" electron in the first two excited singlet states is highly localized by the CI procedure to the N–Cl bond. This orbital, designated σ^*_{NCl}, is shown for the lowest excited state in Figure 4. The corresponding orbital for the second lowest excited singlet state is not noticeably different and is not shown. In view of the strongly antibonding nature of the excited electron distribution of the two lowest excited singlet states, these states should be dissociative, losing atomic chlorine. The third and fourth excited states are made up of two principal components: state 3, $\pi^*_{ONCl}{}^* \rightarrow \sigma^*_{NO}$ and $n_{ONCl} \rightarrow \sigma^*_{ONCl}$; state 4, $\pi^*_{ONCl} \rightarrow \sigma^*_{NO}$ and $n_{ONCl} \rightarrow \sigma^*_{NCl}$. The terminal orbitals, σ^*_{NO} and σ^*_{ONCl}, shown in Figure 4, are antibonding across the NO bond of the three-membered ring. These states are calculated to be well separated from the lower states and from each other, although the absolute values of the excitation energies are probably exaggerated by the perturbative CI procedure.

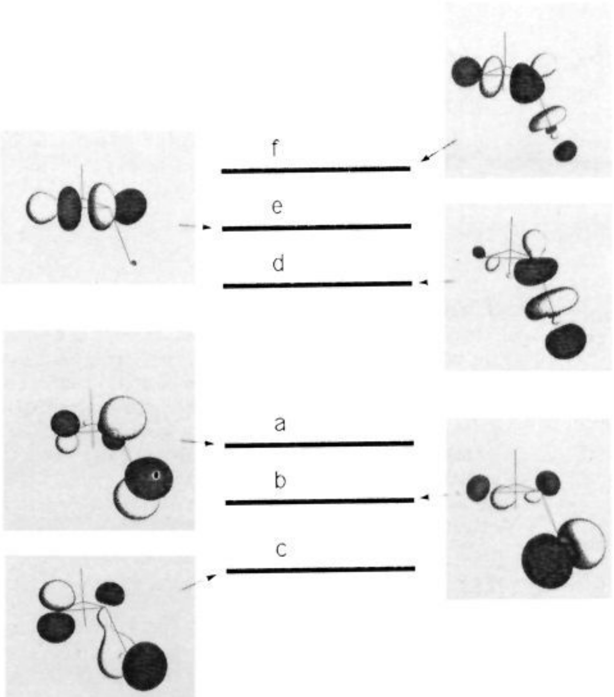


Figure 4. MOs of **3** at contour 0.10: (a) π^*_{ONCl}(HOMO), (b) $3p_{Cl}$, (c) n_{ONCl}(HOMO), (d) σ^*_{NCl}, (e) σ^*_{NO}, (f) σ^*_{ONCl}. See the text and Table IV for a discussion of the role of these orbitals in the excited states.

The derived transition properties of (2*S*)-**3** are collected in Table IV. The lowest energy transition is found to have a positive rotatory strength, and a moderately large oscillator strength. The transition to the second lowest excited singlet state also has a positive rotatory strength of about the same magnitude but a substantially weaker oscillator strength. The two transitions are separated in energy by 0.72 eV. Taking into account that (+)-(2*R*)-**1** has the opposite absolute configuration at N, the calculated results are in substantial agreement with the results of the deconvolution of the UV and CD spectra of (+)-(2*R*)-**1** shown in Figure 2. In **1**, the weaker second transition is separated from the first by 0.58 eV.

Deconvolution of the experimental UV and CD spectra of (+)-(2*R*)-**1** (Figure 2, Table I) suggests the presence of a transition with moderate oscillator strength and weak rotatory strength to a third excited singlet state ~0.56 eV above the second state, characteristics that generally agree with those computed for the third transition of **3** (Table IV). A fourth transition further in the UV than could be observed experimentally is calculated to have a large oscillator strength and a large rotatory strength of sign opposite to that observed for the first transition. This is the transition that is most likely responsible for the fact that (2*R*)-**1** is dextorotatory at long wavelength while the first two bands in the CD spectrum have negative rotatory strength.