STEREOCHEMICAL AND STRUCTURAL FEATURES OF N-METHOXYAZIRIDINES. STRUCTURES OF cis- AND trans-AMIDES OF THE MONOETHYL ESTER OF 1-METHOXYAZIRIDINE-2,2-DICARBOXYLIC ACID*

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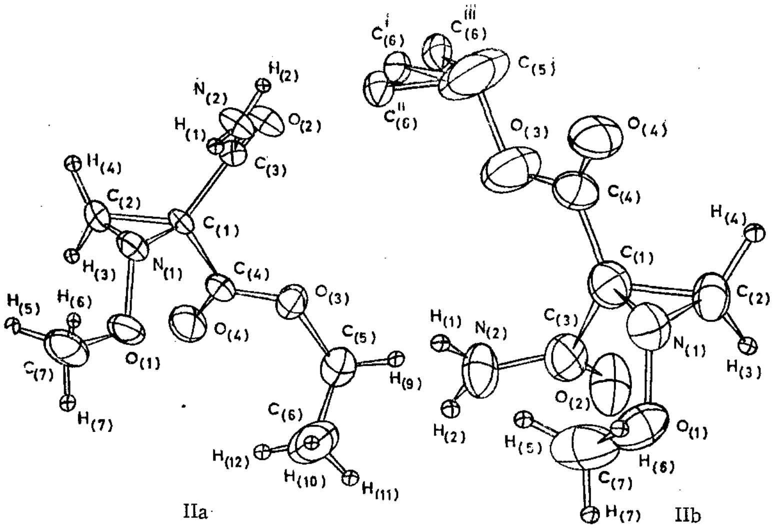
Features of the structures of N-methoxyaziridines have been considered on the basis of the results of x-ray structural analysis, ^{13}C NMR spectroscopy, qualitative MO theory, and the "secondary orbital rehybridization" method. The causes of the configurational and chemical stability of the N-methoxyaziridines, the orientation of the unshared electron pairs of the N and O atoms relative to the O—N bond and the O—C bond of the methoxy group, the structural and conformational manifestation of the interaction of a π-acceptor with the aziridine ring, the laws of the change in the exocyclic valence angles at the carbon atoms of the aziridine ring, and the close values of the SSCCs of the carbonyl carbon atoms with the protons of the ring are discussed.

The trans-stereospecificity of nucleophilic substitution in the ester group of diethyl 1-methoxyaziridine-2,2-dicarboxylate (I) [2] has been shown unambiguously by an x-ray structural analysis of the product of its monoamidation (IIa) and of the corresponding isomer (IIb) [3]. In the present paper we analyze features of the structure of N-methoxyaziridines on the basis of the results of x-ray structural analysis and ^{13}C NMR spectroscopy. The general forms of molecules of (IIa) and (IIb) are shown in Fig. 1. The bond lengths and valence angles are given in Table 1, the main crystallographic characteristics and coordinates of the atoms having been published previously [3].



IIa IIb

Fig. 1. The (IIa) and (IIb) molecules with the 30%-probability ellipsoids of the thermal vibrations of the nonhydrogen atoms.

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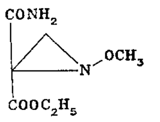
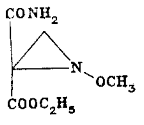
TABLE 1. Bond Lengths (Å) and Valence Angles (deg) in the (IIa) and (IIb) Molecules

Parameter	IIa	IIb	Parameter	IIa	IIb
O(1)—N(1)	1,447 (2)	1,434 (4)	N(1)C(1)C(4)	117,6 (2)	110,5 (3)
O(1)—C(7)	1,417 (3)	1,437 (6)	C(2)C(1)C(3)	119,4 (2)	117,3 (3)
O(2)—C(3)	1,230 (2)	1,230 (5)	C(2)C(1)C(4)	118,4 (2)	115,9 (3)
O(3)—C(4)	1,324 (3)	1,312 (5)	C(3)C(1)C(4)	115,3 (2)	120,6 (3)
O(3)—C(5)	1,463 (3)	1,489 (7)	N(1)C(2)C(1)	60,8 (2)	61,5 (2)
O(4)—C(4)	1,194 (2)	1,206 (5)	N(1)C(2)H(3)	115 (2)	117 (2)
N(1)—C(1)	1,482 (2)	1,503 (4)	N(1)C(2)H(4)	114 (1)	112 (2)
N(1)—C(2)	1,459 (3)	1,450 (5)	C(1)C(2)H(3)	114 (2)	119 (2)
N(2)—C(3)	1,298 (2)	1,311 (4)	C(1)C(2)H(4)	121 (4)	116 (2)
N(2)—H(1)	0,89 (2)	0,86 (5)	H(3)C(2)H(4)	119 (2)	119 (2)
N(2)—H(2)	0,79 (2)	1,03 (3)	O(2)C(3)H(2)	125,5 (2)	124,4 (4)
C(1)—C(2)	1,468 (3)	1,490 (4)	O(2)C(3)C(1)	117,4 (2)	120,2 (3)
C(1)—C(3)	1,512 (2)	1,517 (5)	N(2)C(3)C(1)	117,1 (2)	115,4 (4)
C(1)—C(4)	1,502 (3)	1,487 (5)	O(3)C(4)O(4)	125,5 (2)	124,1 (4)
C(2)—H(3)	0,94 (2)	1,03 (4)	O(3)C(4)C(1)	110,0 (2)	111,9 (4)
C(2)—H(4)	0,96 (2)	1,09 (4)	O(4)C(4)C(1)	124,5 (2)	123,9 (4)
C(5)—C(6)	1,493 (3)		O(3)C(5)C(6)	110,7 (2)	
C(5)—C(6′)		1,39 (2)	O(3)C(5)H(8)	111 (1)	
C(5)—C(6″)		1,39 (2)	O(3)C(5)H(9)	108 (2)	
C(5)—C(6‴)		1,40 (2)	C(6)C(5)H(8)	112 (1)	
C(5)—H(8)	1,03 (2)		C(6)C(5)H(9)	103 (2)	
C(5)—H(9)	1,02 (3)		H(8)C(5)H(9)	112 (3)	
C(6)—H(10)	1,07 (3)		O(3)C(5)C(6′)		111,0 (9)
C(6)—H(11)	0,95 (5)		O(3)C(5)C(6″)		107,2 (8)
C(6)—H(12)	1,00 (5)		O(3)C(5)C(6‴)		104 (4)
C(7)—H(5)	1,00 (3)	1,05 (7)	C(5)C(6)H(10)	111 (2)	
C(7)—H(6)	0,99 (3)	1,07 (7)	C(5)C(6)H(11)	102 (2)	
C(7)—H(7)	0,95 (3)	1,03 (6)	C(5)C(6)H(12)	104 (3)	
N(1)O(1)C(7)	106,5 (2)	107,4 (4)	H(10)C(6)H(11)	119 (3)	
C(4)O(3)C(5)	117,5 (2)	114,6 (4)	H(10)C(6)H(12)	114 (3)	
O(1)N(1)C(1)	108,3 (2)	109,7 (3)	H(11)C(6)H(12)	103 (4)	
O(1)N(1)C(2)	110,0 (2)	108,7 (3)	O(1)C(7)H(5)	115 (2)	118 (4)
C(1)N(1)C(2)	59,9 (2)	60,6 (2)	O(1)C(7)H(6)	113 (2)	107 (3)
C(3)N(2)H(1)	127 (1)	119 (3)	O(1)C(7)H(7)	105 (2)	112 (3)
C(3)N(2)H(2)	118 (1)	122 (2)	H(5)C(7)H(6)	100 (3)	101 (5)
H(1)N(2)H(2)	114 (2)	118 (3)	H(5)C(7)H(7)	107 (3)	118 (5)
N(1)C(1)C(2)	59,3 (2)	58,0 (2)	H(6)C(7)H(7)	118 (3)	97 (5)
N(1)C(1)C(3)	115,3 (2)	118,9 (3)			



IIb



IIa

According to results of x-ray structural analysis, all N-methoxyaziridines are characterized by a higher degree of pyramidal nature of the bonds of the nitrogen atom (the angle φ' in Table 2) than other aziridines [4]. This is due to the increase in the s-nature of the hybrid orbital of the unshared electron pair (UEP) of the nitrogen atom under the influence of the electronegative substituent MeO [7] ("secondary rehybridization model") which, in its turn, leads to an increase in the configurational and chemical stabilities of the N-alkoxyaziridines which have been obtained in the form of stable optical [4] and geometrical [2, 8] isomers. Another reason for the increase in the configurational stability of the N-alkoxyaziridines is the destabilization of the transition state of the inversion of the nitrogen atom through an increase in the repulsion of the UEPs of the N and O atoms.

A skew conformation of the methoxy group relative to the UEP of the nitrogen atom is characteristic for all N-alkoxyaziridines (Fig. 2, angle τ in Table 2). To explain the reason for this let us consider the interaction of the UEPs of the oxygen atom ($n_p(O)$ and $n_\sigma(O)$) with the highest occupied molecular orbitals (MOs) of the aziridine ring (Fig. 3).* Starting from the assumption that orbitals close in symmetry and energy overlap effectively, two interactions are isolated: $n_p(O)$—n(N) and $n_\sigma(O)$—n(N). Both interactions are destabilizing (four-electron systems). At τ = 0° the $n_p(O)$—n(N) interaction (repulsion) is a minimum, while the $n_\sigma(O)$—n(N) interaction is a maximum. At τ = 90°, the opposite situation arises. The energy

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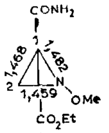
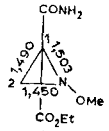
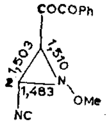
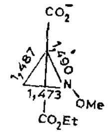
*A purely qualitative consideration of sulfonylaziridine has been given by Kost and Raban [11]

TABLE 2. Inversion ($\Delta G^{\neq}$) and Structural Parameters of N-Methoxyaziridines

Parameter	 IIa	 IIb	 III	 IV
$\Delta G^{\neq}$, kcal/mole[a]	31,0	30,0	33,9	37,9
φ', degrees[b]	67,7	67,6	69,0	69,8
h, Å[c]	0,75	0,75	0,77	0,77
N—O, Å	1,447 (2)	1,434 (4)	1,452 (3)	1,443 (6)
τ, degrees[d]	−44,4	−28,9	−48,3	35,4
δ_{trans}, degrees[e]	−46,5	−6,9	−3,3	−40,0
δ_{cis}, degrees[e]	37,3	62,4	—	61,9
$\angle C^{\text{trans}}C(1)N$, deg.	115,3 (2)	110,5 (3)	112,9 (3)	117,7 (4)
$\angle C^{\text{trans}}C(1)C(2)$, deg.	119,4 (2)	115,9 (3)	115,7 (3)	120,7 (4)
$\angle H^{\text{trans}}C(2)N$, deg.	114 (1)	112 (2)	111 (2)	—
$\angle H^{\text{trans}}C(2)C(1)$, deg.	121 (1)	116 (2)	121 (2)	—
Reference	Present work		[5]	[4]

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[a] The values of $\Delta G^{\neq}$ for the aziridines (III) and (IV) were obtained from the graphical relation $\Delta G^{\neq} = f(\varphi')$ [6]. [b] φ' is the angle of inclination of the N—O bond to the plane of the ring. [c] h is the height of the N pyramid. [d] τ is the torsional angle C_{Me}—O—N center of the $C_{(1)}$—$C_{(2)}$ bond (the reference point is the trans orientation of C_{Me}—O relative to N center of the $C_{(1)}$—$C_{(2)}$ bond; the positive reaction is the deviation of the C_{Me}—O bond on clockwise rotation around the O—N bond). [e] δ is the torsional angle O=C—$C_{(1)}$ center of the N—$C_{(2)}$ bond (the reference point is the cis orientation of O=C relative to $C_{(1)}$ center of the N—$C_{(2)}$ bond, and the positive direction is the rotation of O=C in the $C_{(2)}$ direction); the symbols trans and cis characterize the orientation of the C-substituent relative to the MeON group.

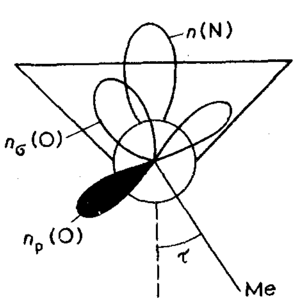


Fig. 2

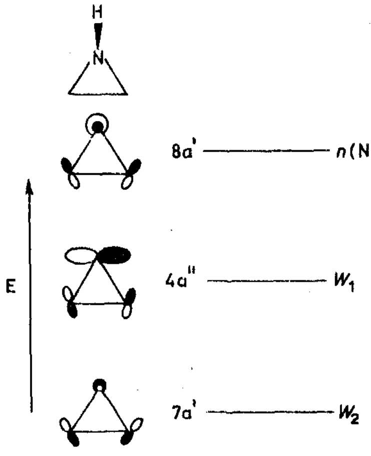


Fig. 3

Fig. 2. Orientations of the unshared pairs of the N and O atoms in N-methoxyaziridines (O→N Newman projection).

Fig. 3. Diagram of the highest occupied molecular orbitals of aziridine according to the results of nonempirical calculations [9]; W_1 and W_2 are Walsh-type orbitals [9, 10].

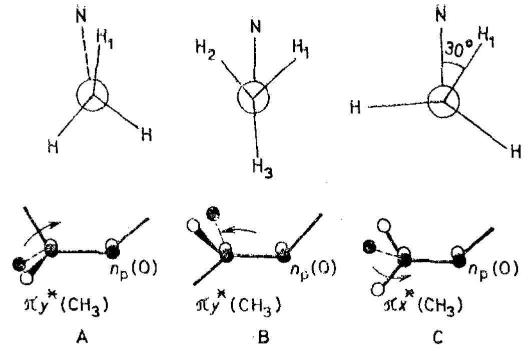
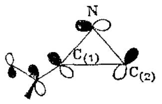


Fig. 4. Suggested interaction of $n_p(O)$ with the group nonbonding orbitals [13] of the Me group (with π^*_y — A and B; with π^*_x — C) [12]. The arrows show the rotation of the C_3 axis of the Me group relative to the O—C bond (structural manifestation of superconjugation).

of the $n_p(O)$—n(N) repulsion is greater than the $n_\sigma(O)$—n(N) interaction; and therefore in the free N-methoxyaziridine molecule τ will be less than 45°. A similar situation is realized for the molecules of (IIa, IIb, and IV) (Table 2). It must be mentioned that with increase in τ, the N—O bond lengthens reaching its greatest value in the nitrile (III) — 1.452(3) Å at $\tau = -48.3°$. It is possible that this tendency is connected with an enhancement of the $n_p(O)$—n(N) repulsion with an increase in τ. In this case, the experimental results characterize the process of the rotation of the methoxy group — an increase in the length of the N—O bond with a rise in the degree of $n_p(O)$—n(N) eclipsing. It is also not excluded that the proximity of the methoxy group to the cis-substituent in the nitrile (III) as compared with the amide (IIb) (the $O...C_{cis}$ distances are 2.612 and 2.721 Å, respectively) leads to a slight lengthening of the N—O bond in the molecule of (III).

The next important conformational feature of the N-methoxyaziridines (IIa and b and III) is the same trans orientation of one of the hydrogen atoms of the methoxy group relative to the N—O bond.* Let us consider three possible conformations from the point of view of the minimum in the energy of the nonvalent repulsive interactions and with the partial delocalization of $n_p(O)$ in the nonbonding orbitals of the CH_3 group [12]† by the analysis of the structural consequences of the n—π^* (CH_3) interaction [13] (Fig. 4). Conformation A is unfavorable, since the propinquity of $H_{(1)}$ to N that exists in the cis orientation must rise when superconjugation exists. Conformation C is more favorable, since the N—O—C—$H_{(1)}$ torsional angle is now 30° and possible superconjugation must lead to a smaller approach of $H_{(1)}$ to N than in conformer A. The most favorable conformation is B, in which the $H_{(1)}$ and $H_{(2)}$ atoms are at the greatest distance from N (the N—O—C—$H_{(1)}$[$H_{(2)}$] torsional angle is 60°), and possible superconjugation leads to an increase in the distance between $H_{(1)}$, $H_{(2)}$, and N. The observed conformational constancy of the MeOH groups in the crystals of compounds (IIa and b and III) is apparently due to the nonvalent interactions that have been considered and to the stereoelectronic effect.

Within the framework of the qualitative MO theory, let us consider the laws of the change in the bond lengths of the aziridine ring under the influence of a π-acceptor. In an aziridine with a π-acceptor at $C_{(1)}$, in addition to the n(N), W_1, and W_2 orbitals, an orbital of the $W_1^{C_{(1)}}$ type with bonding orbitals will apparently be realized in the $C_{(1)}$—N and $C_{(1)}$—$C_{(2)}$ bonds, and with antibonding orbitals in the N—$C_{(2)}$ bond.



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*The conformation of the MeO group in the anion (IV) is not considered, since the hydrogen atoms are localized approximately.

†Features of the structure of the Me—X═Y (where X = CH, N; Y = CH_2, NH, O) of methylborane and methylamine have been interpreted with the aid of hyperconjugation with the participation of the methyl group [13].

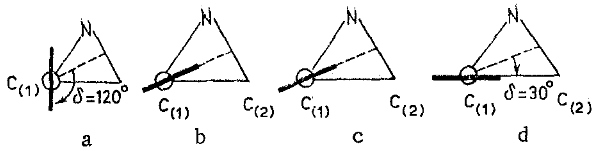

Fig. 5. Torsional angles of unsaturated groups corresponding to the maximum overlap of the antibonding orbitals of the π-acceptor with the occupied MOs of aziridine. The structural manifestation of this interaction is shown in parentheses. The heavy line is projection of the plane of the π-acceptor along the exo C—C bond: a) W_1 (bonding region)—$\pi^*_{C=O}$ interaction [$\delta \approx 120°$ (—60°), lengthening of the N—C bond]; b) $W_1^{C(1)}$ —$\pi^*_{C=O}$ ($\delta \approx 0°$, lengthening of the N—$C_{(1)}$ and $C_{(1)}$—$C_{(2)}$ bonds, shortening of the N—$C_{(2)}$ bond); c) W_2—$\pi^*_{C=O}$ ($\delta \approx 0°$, lengthening of the C—C bond); d) W_1 (antibonding orbital)—$\pi^*_{C=O}$ [$\delta \approx 30$ (−150°) , shortening of the C—C bond].

At the same time, by analogy with cyclopropane derivatives [14, 15], the molecule is stabilized through the delocalization of the electron density from the bonding and antibonding sections of the occupied $W_1{}^{C(1)}$ orbital into the free MO of the π-acceptor, which will lead to a lengthening of the $C_{(1)}$—N and $C_{(1)}$—$C_{(2)}$ bonds and to a shortening of the N—$C_{(2)}$ bond. Figure 5 shows the torsional angles (δ_{max}) characterizing the conditions of maximum overlap of the orbitals of the aziridine ring and of the π-acceptor and it gives the structural manifestations of the interactions. We shall consider an interaction "strong" if the experimental value of δ (Table 2) lies in the section $\delta_{max} \pm 30°$. The π-acceptor influence of the amide group is small in comparison with that of the ester group, and therefore it can be neglected. The basic details of the orbital interaction are as follows. In the amide (IIb), the "strong" $W_1{}^{C(1)}$—$\pi^*_{C=O}$ (δ = —6.9°) interaction will lead to a lengthening of the near and to a shortening of the remote N—C bond as compared with unsubstituted aziridine (C—C 1.481; C—N 1.475 Å) [16]. The greatest difference in the lengths of the N—C bonds for N-alkoxyaziridines is seen in compound (IIb) — 0.05 Å. In the alkoxyaziridine (IIa) there is a "nonstrong" $W_1{}^{C(1)}$—$\pi^*_{C=O}$ interaction, but the $C_{(1)}$—$C_{(2)}$ bond is shortened because of the "strong" W_1 (antibonding)—$\pi^*_{C=O}$ interaction (δ = 37.3°). In the molecule (IV), the "nonstrong" $W_1{}^{C(1)}$—π^*_{COO} W_1(bonding)—π^*_{COO} (δ = —40°) interactions lead to a slight lengthening of the $N_{(1)}$—$C_{(1)}$ bond. In the case of the nitrile (III), there is a direct proof of the π-acceptor effect of the nitrile group in relation to the aziridine ring: The nonlinearity of the C—C≡N fragment (176.7(4)°) shows an eclipsing of the π*-orbitals [17] by the C≡N bond with localization mainly on the C atom. In the molecule of (III), the "strong" $W_1{}^{C(1)}$—$\pi^*_{C=O}$ (δ = —3.3°) and $W_1{}^{C(2)}$—$\pi^*_{C\equiv N}$ (δ = 170°) interaction leads to a lengthening of the C—C bond as compared with the other alkoxyaziridines. The difference between the N—C bonds in this case apparently indicates that a PhCOCO substituent is a stronger π-acceptor than CN.* Thus, the interaction of a π-acceptor substituent with the aziridine ring depends on their mutual orientation. The orbital interaction considered also shows the influence of the exo C—C bond. In the amide groups of the isomers (IIa) and (IIb), where the orbital interaction is insignificant, the length of the $C_{(1)}$—$C_{(3)}$ bond (≈1.515 Å) is approximately the same as in acetamide [19], and the covalent radius of the carbon atom of the aziridine ring is, consequently, ∼0.77 Å (sp^3-hybridization of the C in accordance with [7]). The shortening of the exo C—C bond for all the ester groups and the carboxy groups by approximately 0.02 Å in comparison with C_{sp^3}—C_{sp^2} (CO_2Et) 1.525 Å [20] and C_{sp^3}—C_{sp^2} (CO_2^-) 1.555 Å [21] may be considered as a confirmation of orbital interaction.

It is possible to evaluate the order of the energy of the W—$\pi^*_{C=O}$ interaction. For the molecules of (IIa) and (IV) and the amide group of (IIb), the angles of rotation of the C-substituents are determined by the nature of the intermolecular hydrogen bonds. For the nitrile (III) and the ester group of compound (IIb) (in the absence of hydrogen bonds), the most favorable bisector conformation of the substituent ($\delta \approx 0°$) is apparently realized. Consequently, the energy of the W—$\pi^*_{C=O}$ interaction is less than the energy of the N—H...O hydrogen bonds.

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*It has been shown that in relation to the cyclopropyl group CO is a considerably stronger π-acceptor than CN [18].

TABLE 3. Parameters of the ^{13}C NMR Spectra of the Isomers (IIa and b)

Compound	Solvent	δ, ppm[a] $J_{^{13}CH}$, Hz)						
		CH_3	CH_3O	CH_2O	CH_2N	CN	CO_2	CON
IIa	$CDCl_3$	14,06 (127,6) ($^2J=3,8$)	60,92 (144,3)	62,43 (148,0)	41,38 (173,9 and 179,4)	50,53	163,96	167,48
	CD_3OD	14,38 (127,6) ($^2J=3,7$)	61,23 (142,4)	63,30 (147,2)	42,02 (172,0 and 179,4)	52,45	165,14 ($^3J_{C-CH_2}=3,8$, $^3J_{C-H_{(3)}}=$ $=^3J_{C-H_{(4)}}=3,7$)	170,78 ($^3J_{C-H_{(3)}}=$ $=^3J_{C-H_{(4)}}=3,7$)
IIb	$CDCl_3$	13,98 (125,9) ($^2J=3,8$)	61,13 (145,0)	62,58 (152,6)	41,50 (172,1 and 179,3)	48,66	168,13	163,06
	CD_3OD	14,24 (127,6) ($^2J=3,7$)	61,02 (142,6)	63,18 (152,8)	42,24 (170,2 and 177,6)	51,59	168,61 ($^3J_{C-CH_2}=3,8$, $^3J_{C-H_{(3)}}=$ $=^3J_{C-H_{(4)}}=3,7$)	166,42 ($^3J_{C-H_{(3)}}=$ $=^3J_{C-H_{(4)}}=3,6$)

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[a] NT-360-WB spectrometer (Nicolet, USA) at 90.81 MHz (^{13}C); internal standard TMS.

The general law of the change in the exocyclic valence angles at the C_1 and C_2 atoms — $\angle C^{trans}C_{(1)}N < \angle C^{trans}C_{(1)}C_{(2)}$ and $\angle H^{trans}C_{(2)}N < \angle H^{trans}C_{(2)}C_{(1)}$ (Table 2) — can be explained by two factors. In the first case, the center of electron density in the endo N—C bond, in contrast to the C—C bond, is shifted to the nitrogen atom, which leads to the inequalities $\angle C(H)^{trans}CN < \angle C(H)^{trans}CC$, and $\angle C(H)^{cis}CN < \angle C(H)^{cis}CC$. In the second place, the distance between the exocyclic atoms in the α position is considerably smaller than the sum of the Van der Waals radii, which leads to the necessity for taking nonvalent repulsive interactions into account. The exo C—C bond—UEPN and the C—H bond—UEPN interactions are smaller than the interaction between the exo C—C and the C—H bonds. Consequently, for trans substituents we again obtain the inequality $\angle C(H)^{trans}CN < \angle C(H)^{trans}CC$. For cis substituents, an analysis of the change in the exocyclic valence angles is difficult, since it is necessary to consider three groups of repulsive interactions (C—H and N—O, C—H and exo C—C bond, and N—O and exo C—C bond) and to establish the relative orders of their destabilization. The suggested explanation is confirmed by the results of fine microwave studies of aziridine [16] ($\angle H^{trans}CN = 114.27°$, $\angle H^{trans}CC = 119.32°$), of N-chloroaziridine [22] ($\angle H^{trans}CN = 113.66°$, $\angle H^{trans}CC = 120.38°$), and of ethylene oxide ($\angle HCO < \angle HCC$). The intensification of the inequality on passing from aziridine to N-chloroaziridine is explained by the increase in the electron-accepting nature of the N—Cl bond as compared with the N—H bond. The considerations given explain the observed twisting of the CH_2 group relative to the plane of the ring in aziridine and N-chloroaziridine (87° and 87.7°, respectively) and of the $C_{(1)}C_{(3)}C_{(4)}$ plane relative to the $C_{(1)}C_{(2)}N_{(1)}$ plane in the molecule of (IIb) (86.4°).

In the amide (IIb), the $C_{(6)}$ atom is statistically disordered over three positions. The multiplicities of the positions have been refined: $C_{(6')}$—0.39, $C_{(6'')}$—0.41, $C_{(6''')}$—0.25. The physical sense of the disorder of $C_{(6)}$ is the existence of three rotational isomers relative to the $O_{(3)}$—$C_{(5)}$ bond. The reason for the disorder is the absence in crystals of (IIb) of C—X intermolecular contacts [where C is C—$C_{(6')}$, $C_{(6'')}$, $C_{(6''')}$ and X is O, N, C, H] less than the sum of the Van der Waals radii of the atoms [24].

In order to elucidate the stereospecificity of the SSC constants of the carbonyl carbons with the protons of the ring, we have investigated the ^{13}C NMR spectra of the aziridines (IIa and b). The assignment of the ^{13}C signals was made on the basis of $\delta^{13}C$ and $J_{^{13}CH}$ values. The signals of the carbonyl carbon atoms were assigned with the aid of ^{13}C—{^1H} selective heteronuclear double resonance with successive irradiation of the CH_2O and the 3- and 4-H protons, and also in the light of the changes in the spectra on the exchange of protons in CD_3OD (absence of $^{2}J_{^{13}CNH}$). When the CH_2O protons were irradiated, in the spectrum of the aziridine (IIb) in CD_3OD the ^{13}CO weak-field multiplet (168.61 ppm) and in the isomer (IIa) the high-field ^{13}C multiplet (165.14 ppm) were transformed into triplets. When the 3- or 4-H protons of the ring were irradiated in the spectra of compounds (IIa and b) doublets of triplets were observed from the ester carbonyl atoms, and CO doublets from the amide atoms (Table 3). The results obtained show that the carbonyl carbon atoms in the cis orientation with respect to the UEP of the aziridine nitrogen in the molecules of (IIa and b) are descreened in comparison with trans $C{=}O$, which is in harmony with other results [25]. The close values of the constants of the carbonyl carbon atoms with the protons of the ring are due to the similar $C(CO){-}C_{(1)}{-}C_{(2)}{-}H$ torsional angles (149-150°) in the isomers (IIa and b) and show a weak influence of the UEP on $^{3}J_{^{13}CH}$. Thus, the values of $^{3}J_{^{13}CH}$ for compounds of this type can be used as a stereochemical criterion.

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