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INVESTIGATIONS ON 1-AZABICYCLIC COMPOUNDS. 25*. STEREOCHEMISTRY, HYDROGEN BONDS, AND GAS-LIQUID CHROMATOGRAPHY OF PYRROLIZIDINE ALCOHOLS

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Data have been summarized of several studies on the separation of isomeric pyrrolizidine alcohols by GLC using liquid polar stationary phases. It was shown that the order of emergence of isomers from the chromatographic column is determined to a significant extent by competition of intermolecular hydrogen bonds formed in the sorbate–sorbent systems and intramolecular hydrogen bonds in the molecules of the same pyrrolizidine alcohols. The preference for one or other type of hydrogen bond depends on the stereochemistry of the pyrrolizidine alcohols. Analysis of the geometric conditions for the formation of intramolecular hydrogen bonds in the investigated compounds in conjunction with chromatographic resolution data enables their configurations to be assigned. The anomalously short retention times of highly strained 5-hydroxyalkyl-3-methylpyrrolizidines are explained by the existence in them of a bicyclic conformation predominantly with a trans linkage and with favorable geometric conditions for forming intramolecular hydrogen bonds in them.

Keywords: azabicyclic compounds, pyrrolizidine alcohols, GLC, configurational assignment.

1. GAS-LIQUID CHROMATOGRAPHY AND HYDROGEN BONDS

First Attempts to Use GLC to Solve Stereochemical Problems. Aim and Problem of the Investigation.

The hydrogen bond (HB) between the sorbate and the stationary phase is one of the most important factors determining the retention time in GLC [2-4]. From a comparison of the geometry of isomer molecules it is possible to construct a picture of the relative stability of their HB with the polar stationary phase and to solve the problem of which of the isomers forms intramolecular HB, from which the order of their emergence from a column is readily explained. The opposite approach is also possible. Comparing retention times or volumes and analyzing comparatively the geometry of the molecules of the isomers, in particular an assessment of the geometry of the hydrogen bridge, may lead to their configurational assignment. GLC was applied for the first time to solve a similar stereochemical problem in 1959 in an investigation of compounds of the borneol series [5]. The authors of this work reckoned that the GLC method may be considered as an important addition to IR

* For Part 24 see [1].

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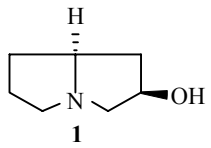
spectroscopy in the study of intramolecular HB. Later the fruitfulness of the GLC method was demonstrated in the analysis of the stereochemistry of indolizidine and quinolizidine alcohols [6,7] and 2-hydroxypyrrolizidines (**1** and **2**) [8]. Data have also been described on the GLC of 1-hydroxymethylpyrrolizidines (**3** and **4**) [9].

In the present work we have studied the behavior on GLC of the isomeric pyrrolizidine alcohols **5** and **6** [10], **7-10** [10], **11-14** [11], **15** and **16** [12], and **17-20** [12].



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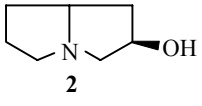

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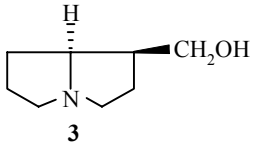

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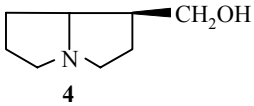

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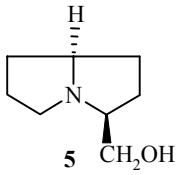

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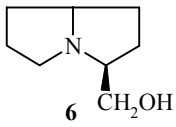

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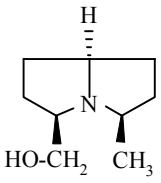

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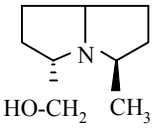

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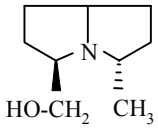

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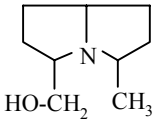

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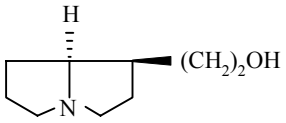

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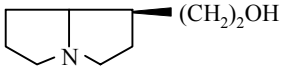

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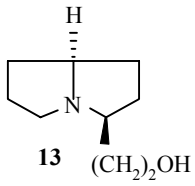

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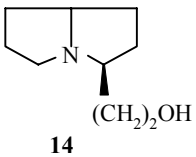

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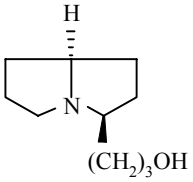

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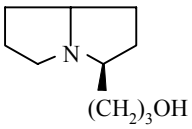

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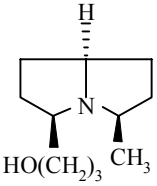

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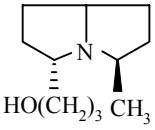

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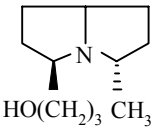

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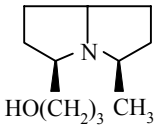

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The problem of the investigation comprised clarification of the dependence of the retention time of isomers on their stereochemistry and, in particular, on the geometric conditions of forming intramolecular HB or intermolecular HB between the aminoalcohol molecules and the liquid polar stationary phase.

2. GEOMETRY OF THE HYDROGEN BOND AND ITS EFFECT ON THE RETENTION OF A COMPOUND ON GLC ON A POLAR STATIONARY PHASE

We consider the general case of the interaction of isomeric aminoalcohols **A** and **B** with a polar stationary phase **C** (see Fig. 1). Isomer **A** has an intramolecular HB, but because of its geometry isomer **B** is not able to form an intramolecular HB.

The more stable the intramolecular HB in compound **A** the weaker will be the energy of its specific interaction with phase **C** (due to the formation of complexes **A···C** with intermolecular HB) and the lower will be its retention time [4]. Isomer **B** forms complexes **B···C** with phase **C** with intermolecular HB and it is easy to see that the interaction energy of **A** with **C** will be lower than that of **B** with **C**, since in the first case it is necessary to consume energy to break intramolecular HB to form intermolecular HB [4].

It must be kept in mind that the stability of intramolecular HB is a function of many parameters: the basicity of the acceptor of protons, the acidity of the hydroxyl [13,14], and the geometry of the hydrogen bridge [15].

Also to be considered are the distance *l* between the atom donating protons (O) and the atom accepting protons (for example N), and also the angle sizes α and β shown for alcohols of the type $HO(CH_2)_nN$ **21** for example in Fig. 2 [15].

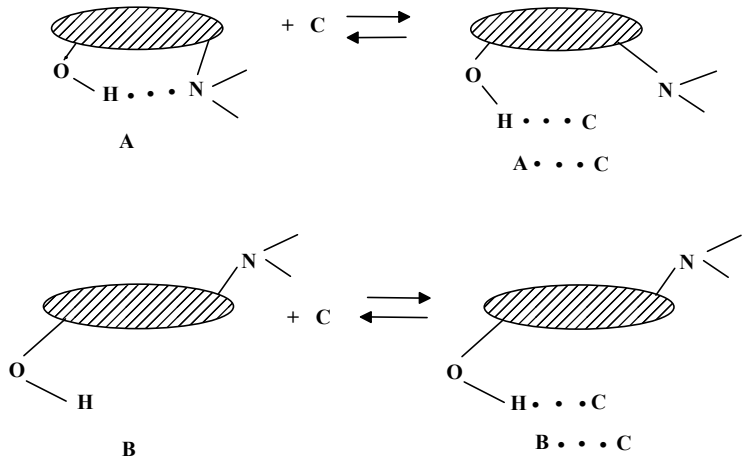

Fig. 1.

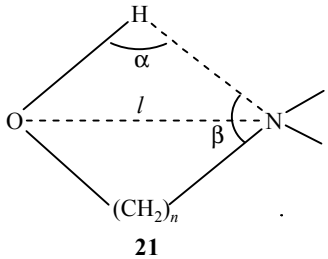

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Fig. 2.

The closer the disposition of the O, H, and N atoms to linear then the more stable is the intramolecular HB [15]. An intermolecular HB in the crystalline state has a tendency to be formed in the direction of the unshared electron pair [16]. It is evident that the rule found for intermolecular HB is fully applicable to intramolecular HB, i.e. the most stable bond is formed when the direction of the HB coincides with the direction of the axis of the unshared electron pair of the acceptor N [17].

We assume that it is more convenient to use only two parameters when describing the geometry of a hydrogen bridge, the distance *l* and the angle α as was done in [18]. The angle α is formed by the line of the OH bond and by the continuation of the axis of the unshared electron pair of the acceptor of protons. These parameters are shown in Fig. 2 for one case of amino alcohols.

The different variants are illustrated in Figs. 3-6 for the mutual disposition (irrespective of *l*) of the hydroxyl group and the unshared electron pair of the nitrogen atom, from the most favorable (α = 180°), through intermediate (180° > α > 0°), to cases of their reverse direction (α < 0°)*, (α = -180°), at which intramolecular HB are impossible.

The optimum O···N distance (*l*) is approximately 2.8 Å [18,19]. An increase in this distance leads to a weakening of the HB.

Isomers of type A with intramolecular HB will therefore always leave the column earlier than isomers of type B which do not form intramolecular HB. An assessment of the stability of the intramolecular HB in a series of isomeric molecules of type A, according to the initial geometric condition for forming intramolecular HB, enables the order of their emergence from a column to be predicted. On the other hand, finding the order of emergence of isomers by experiment and analyzing the geometry of their intramolecular HB in models may give an opinion as to their configurations.

3. CONFORMATIONS OF PYRROLIZIDINE ALCOHOLS

Six basic conformations are known for pyrrolizidine bicyclic compounds, *viz*. *cis*-linked, open, half-folded, folded, *trans*-linked, and twisted [20]. For unsymmetrically substituted pyrrolizidines, such as 3-alkylpyrrolizidines [21], the number of conformations is increased since in this case two half-folded and two twisted conformations already exist. When analyzing the conditions of forming intramolecular HB in

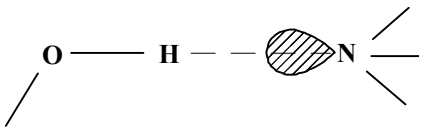


Fig. 3.

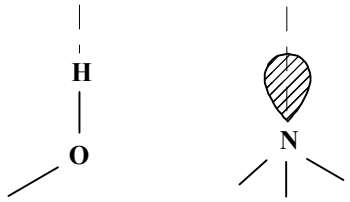


Fig. 4.

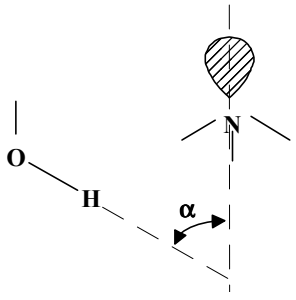


Fig. 5.

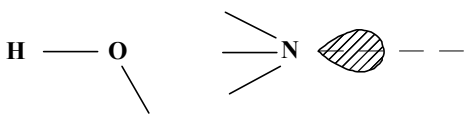


Fig. 6.

pyrrolizidine alcohols the nonbonding interactions and angular strains in the actual bicycle have been taken into account [21]. Energetically, folded and twisted conformations disadvantageous for nonbonded interaction and angular strain are disregarded, since they do not obtained additional stabilization on forming intramolecular HB compared with others.

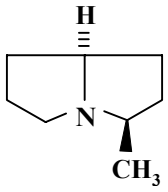
The actual geometric parameters α and *l* of intramolecular HB were found by direct measurement on molecular models. These measurements are somewhat arbitrary because of the difficulties of selecting optimal conformations of hydroxyethyl and hydroxypropyl groups. None the less we suppose they reflect the order of the size of angles α and distances *l* and assist making a qualitative judgement on the relative stability of intramolecular HB in isomers or on establishing their absence.

In one of the half-folded conformations of pyrrolizidine alcohols the geometry of the intramolecular HB is the same as in the open conformation. Consequently when measuring on models of compounds one of two half-folded conformations is taken, where the orientation of the hydroxyl or hydroxyalkyl group is changed from pseudoequatorial to pseudoaxial or vice versa in comparison with the open conformation.

As is known substituted pyrrolizidines are subdivided into unstrained, weakly strained, and highly strained [22-24]. Each of the unstrained pyrrolizidine alcohols **6**, **10**, **12**, **14**, **16**, and **20** are considered in the open and half-folded conformations respectively with pseudoequatorial and pseudoaxial hydroxyalkyl groups.

The 3-substituted and 3,5-disubstituted pyrrolizidines occupy a special position in conformational analysis since in one of the isomers in the *cis*-linked conformations significant nonbonding interactions are observed for the substituent at the third carbon atom with the hydrogen atoms or other substituent at the fifth carbon atom. The strain from the nonbonding interactions is reduced on inversion of the nitrogen atom and on transfer of the bicyclic system into a *trans*-folded conformation, having however a high angular strain [20,21,24].

For the weakly strained *cis*-3,8-H-3-methylpyrrolizidine (**22**) the *trans*-linked form (**22a**) was detected in a mixture of equilibrium conformations [22,23,25].



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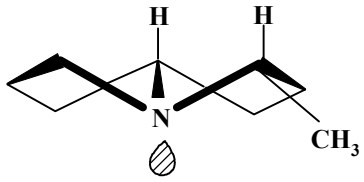


22a

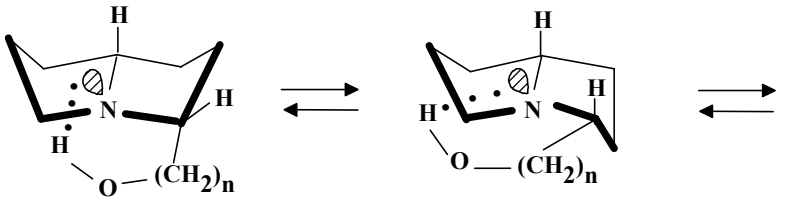
Therefore in the case of the 3-hydroxyalkylpyrrolizidines **5**, **13**, and **15** measurements were carried out for the open (**5a**, **13a**, and **15a**), the half-folded (**5b**, **13b**, and **15b**), and the *trans*-linked (**5d**, **13d**, and **15d**) conformations (Scheme 1).

The conformations **5c**, **13c**, and **15c** were not taken into consideration since the geometry of the intramolecular HB in them is the same as in the conformations of the corresponding **5a**, **13a**, and **15a**.

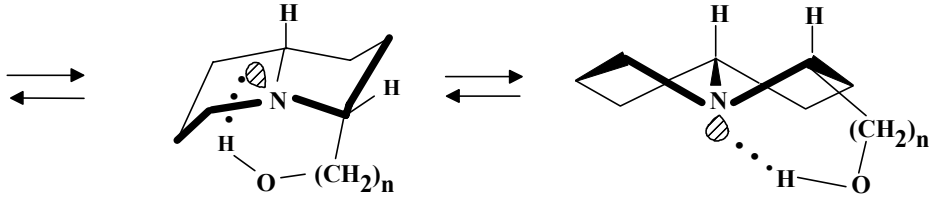
In compounds **1** and **3** substituents are not found beside centers of inversion (nitrogen) and the radical change of the geometry of the bicyclic compound on going from the *trans*-linked form does not weaken significantly the nonbonded interactions. This circumstance excludes consideration of their *trans*-linked forms.

The highly strained pyrrolizidine alcohols **7** and **17**, by analogy with the highly strained *cis*-3,8-H-*cis*-5,8-H-3,5-dimethylpyrrolizidine (**23**) for which the *trans*-linked conformation (**23a**) dominates by no less than 95.8% [25], were considered only in the *trans*-linked forms **7a** and **17a** (Scheme 2).

Scheme 1



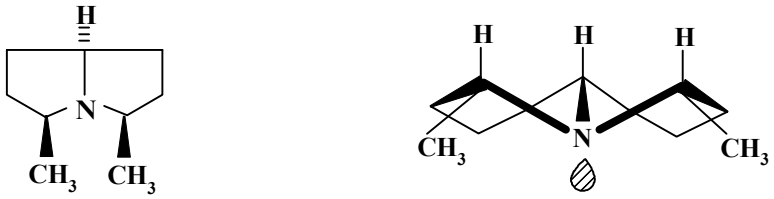
5a, **13a**, **15a** **5b**, **13b**, **15b**



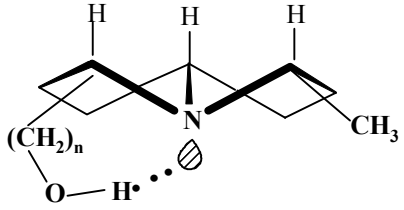
5c, **13c**, **15c** **5d**, **13d**, **15d**

5a-d *n* = 1; **13a-d** *n* = 2; **15a-d** *n* = 3

Scheme 2



23 **23a**



7a, 17a

7a *n* = 1; **17a** *n* = 3

4. DATA ON GLC OF PYRROLIZIDINE ALCOHOLS AND THEIR LINK WITH THE STEREOCHEMISTRY OF THE BASES

The sequences of the emergence on GLC of isomeric pyrrolizidine alcohols from a polyethyleneglycol 20000 column, and the initial geometric parameters α and *l* measured on models, are given in Table 1. In addition to the data obtained by us results described in the literature on the GLC of amino alcohols **1**, **2** [8] and

TABLE 1. Pyrrolizidine Alcohols, Geometric Parameters of Intramolecular Hydrogen Bonds as Measured on Models, and the Sequence of Emergence of Isomers from a Column of Polyethyleneglycol 20000 on GLC

Group of isomers	Compound (isomers are given in order of emergence from the column)	Conformation	Angle α, deg.*	Distance N···O (*l*), Å*
1, **2**	**2**	Open	33	3.2
		Half-folded	<0	3.8
	1	Open	<0	3.8
		Half-folded	<0	3.2
3, **4***[2]	**4**	Open	69	3.8
		Half-folded	82	3.2
	3	Open	<0	4.9
		Half-folded	<0	4.8
5, **6**	**6**	Open	99	2.6
		Half-folded	100	2.6
	5	Open	~10	2.9
		Half-folded	36	2.9
		trans-Linked	85	2.7
7-10	**7**	*trans*-Linked	85	2.7
	10	Open	99	2.6
		Half-folded	100	2.6
	9	Open	99	2.6
		Half-folded	100	2.6
	8	Open	~10	2.9
		Half-folded	36	2.9
11-14	**14**	Open	140	2.5
		Half-folded	133	2.4
	13	Open	75	2.9
		Half-folded	80	3.5
		trans-Linked	125	2.7
	12	Open	110	3.4
		Half-folded	112	2.6
	11	Open	0 or <0*[3]	4.0
		Half-folded	40	4.8
15, **16**	**16**	Open	170	2.3
		Half-folded	170	1.9
	15	Open	100	2.7
		Half-folded	140	2.4
		trans-Linked	180	2.1
17-20	**17**	*trans*-Linked	180	2.1
	20	Open	170	2.3
		Half-folded	170	1.9
	19	Open	170	2.3
		Half-folded	170	1.9
	18	Open	100	2.7
		Half-folded	140	2.4

* The precision of measuring angles α and distances *l* on models of compounds **1-14** was ±5° and ±0.2 Å respectively, and for models of compounds **15-20** ±10° and ±0.3 Å.

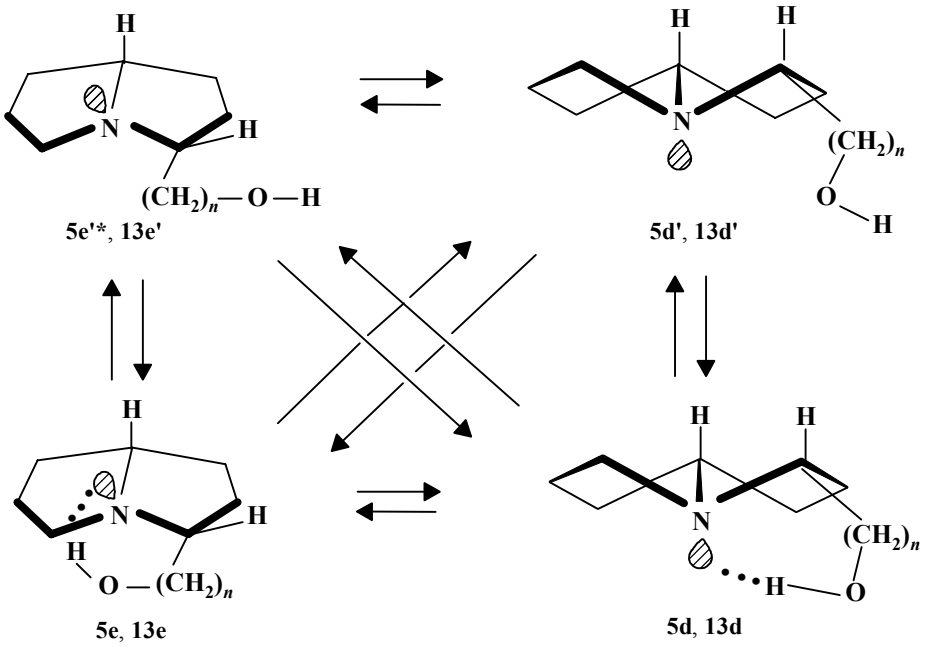
*[2] Polypropyleneglycol adipate (Reoflex 400) was used as polar stationary phase on GLC.

*[3] Depending on the conformation of the $(CH_2)_2OH$ group.

3, **4** [9] are included. Base **2** emerges from the column sooner than isomer **1**, and this is in agreement with the geometric parameters indicating that compound **2** is more inclined to form intramolecular HB than compound **1**. The existence of intramolecular HB in aminoalcohol **2** is confirmed by data of IR spectra [8]. The same applies to the pair of isomers **3** and **4** [9].

Comparison of the geometry of the hydrogen bridge of various conformations of bases **5** and **6** shows that the conditions for forming intramolecular HB are worse in the first than in the second. It should however be noted that in the *trans*-linked conformation **5d** the geometric conditions for forming intramolecular HB are close to those in compound **6**. The intramolecular HB in the *trans*-linked conformation **5d** are evidently a factor stabilizing this conformation, consequently the conformational equilibrium (**5e** ⇄ **5e'**) ⇄ (**5d** ⇄ **5d'**) will be shifted to a larger extent to the right than the analogous conformational equilibrium for base **22** [22,23,25].

Transition from the *cis*-linked conformations **5e** and **5e'** of compound **5** to conformations **5d** and **5d'** radically changes the geometry of the pyrrolizidine system and reduces the dipole moment of the bicyclic compound [26].



5d', **5e**, **5e'** $n = 1$; **13d'**, **13e**, **13e'** $n = 2$

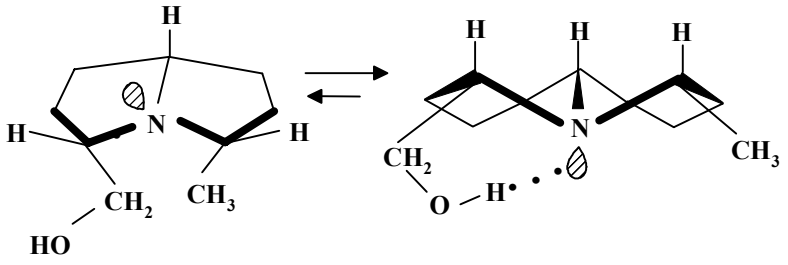
As a result, a negative contribution to the retention time of isomer **5** appears from the difference of nonspecific interactions with the stationary phase of the systems with *cis* and *trans* linking of the rings, reducing this time. In total these factors might guarantee a lower emergence time for isomer **5** if it was *trans*-linked for the most part. The observed order of emergence of isomers shows that the *trans*-linked form of compound **5** is not dominant. This fact is confirmed by the absence of marked Bolman absorption in the IR spectra of compound **5**, which is a characteristic of the predominantly *trans*-linked amino alcohols **7** and **17** [12,24].

Owing to the fact that compound **5** is an equilibrium mixture of *cis*- and *trans*-linked conformations, averaging occurs of the geometric parameters of the intramolecular HB at the three conformations given in Table 1 to $\alpha < 85°$ and 2.7 Å $< l <$ 2.9 Å. Compound **6** therefore forms more stable intermolecular HB with PEG 20000 than does base **5**. This circumstance determines the observed order of emergence of the isomers.

If there would be no *cis-trans* conversion of the pyrrolizidine bicycle and compounds **7-19** existed in the *cis*-linked forms, then they would emerge from the column in the sequence **10, 9, 8, 7** determined by the initial geometry of the intramolecular HB and by factors of the configurational difference at $C_{(3)}$. In reality these

* For simplicity each family of *cis*-linked conformations **5a-5c** are represented by formulas of type **5e'** and **13e'** [20].

isomers leave the column in a different order, *viz*. **7, 10, 9, 8**. The greatest volatility of base **7** is caused by the fact that this compound, due to very strong nonbonding interactions in the *cis*-linked conformations (**7a**), analogous to the highly strained base **23** [20-22,24-27], exists predominantly in the *trans*-linked form **7b**.



7a **7b**

The conformation **7b** is additionally stabilized by the formation of intramolecular HB. Since the initial geometry of the intramolecular HB of compounds **7** and **10** are close to one another according to the model but the type of bicycle linking is different, then it is evident that when considering the order of emergence of the isomers from the column it is necessary to take into account other factors proving to have a weaker effect than HB on the retention of the sorbate in the column. It was shown in [26] that the lower dipole moment and the larger molecular volume of *trans*-linked pyrrolizidines causes them to bind more weakly to the stationary phase than *cis*-linked bases. The difference in retention of isomers **7** and **10** by the column therefore becomes understandable.

As is evident from Table 1 compounds **9** and **10** have the same geometry of the intramolecular HB and their separation is caused by the configurational difference at $C_{(3)}$, as occurs for the epimeric 3-alkylpyrrolizidines [26]. The order of emergence from the column of isomers **8** and **9** is analogous to the order of emergence of compounds **5** and **6** and is interpreted as considered above for the latter pair.

There is considerable interest in the separation of the mixture of the four isomers 1-(2'-hydroxyethyl)- (**11**, **12**) and 3-(2'-hydroxyethyl)pyrrolizidines (**13**, **14**). When discussing the data given in Table 1 it is necessary to bear in mind that compound **13** may be considered as a derivative of base **22**, for which, as was shown above, the presence of the *trans*-linked form **22a** was established in the equilibrium mixture of the conformations [21-23]. Consequently for base **13** there must also be a conformational heterogeneity in the type of linking of the rings (**13e'** ⇄ **13e**) ⇄ (**13d'** ⇄ **13d**). Moreover, as is seen from Table 1, the geometric conditions for forming intramolecular HB in the *trans*-linked conformation **13d** are better than in the *cis*-linked, which leads to some additional stabilization of conformation **13d** compared with the *trans*-linked form **22a** of compound **22**. Starting from this reasoning we may consider that the proportion of *trans*-linked conformation in the mixture of equilibrium conformations of aminoalcohol **13** is greater than in the homologous pyrrolizidine **22**. Not knowing the position of the conformational equilibrium of compound **13** it is impossible to decide in what sequence isomers **12** and **13** will emerge from the column from measurements of the initial geometric parameters of the intramolecular HB in models. The order of emergence of isomers **12** and **13** found experimentally (using a binary mixture of **13** and **14** and a mixture of all four isomers **11-14**) indicates that the averaged value for the energy of the intramolecular HB in each conformation of compound **13** is greater than in compound **12**. The last of the four considered isomers **11-14** leaving a column of PEG 20000 is compound **11.** **A**ccording to the analytical data, compound **11** does not form an intramolecular HB at all or forms an extremely weak intramolecular HB (in the half-folded conformation $\alpha = 40°$, $l = 4.8$ Å) and consequently has the strongest intermolecular HB with the stationary phase.

As is known, compounds with a large value of $\Delta\nu_{OH}$, determined from the IR spectra, have more stable HB, other conditions being equal [15,19]. The order of emergence of isomers **15** and **16** correlates well with the relative stability of the intramolecular HB in these compounds determined from the value of $\Delta\nu_{OH}$. The second

compound has a larger $\Delta\nu_{OH}$ – 495 than the first, where $\Delta\nu_{OH}$ is 457 cm^{-1}. Consequently, as is seen from Table 1, base **16** has a more favorable geometry for the formation of intramolecular HB and a more stable intramolecular HB and emerges from the column before aminoalcohol **15**.

The interpretation of the data on the retention of isomers **17-20** on the column was carried out analogously to that given above for compounds **7-10**. Separate comment is required on the apparent contradiction between the order of emergence of isomers **17** and **20** and the values of their $\Delta\nu_{OH}$ – 465 and 500 cm^{-1} respectively, indicating a somewhat more stable intramolecular HB in the second case. It is however necessary to take into consideration that base **17** behaves as a highly strained pyrrolizidine and by analogy with compound **23** it must exist predominantly in the *trans*-linked form **17a**. This was confirmed by IR and ^{13}C NMR spectroscopy [12].

Regarding the actual difference in the sizes of $\Delta\nu_{OH}$ of the isomers with closely similar initial geometry of their intramolecular HB, it is necessary to bear in mind that in the predominantly *trans*-linked pyrrolizidines nitrogen has a lower basicity than in *cis*-linked bases [27], and consequently, by analogy with other aminoalcohols [13], must have a lower value of $\Delta\nu_{OH}$. The order of emergence of isomers **17** and **20** with close initial parameters of the intramolecular HB and $\Delta\nu_{OH}$ is determined, as in the case of 5-hydroxymethyl-3-methylpyrrolizidines **7** and **10,** by factors linked with the principal differences of the geometry of the bicyclic compound.

EXPERIMENTAL

The synthesis of the pyrrolizidine alcohols **5-20**, the conditions for chromatographing them, recording their IR and ^{13}C NMR spectra were described in [10-12]. Data on the order of emergence from the column on GLC of the isomeric pairs **1**, **2** and **3**, **4** are taken from [8,9] respectively.

Measurements of the geometric parameters of intramolecular HB were carried out on models from Framework Molecular Models (Prentice-Hall Inc., Englewood Cliffs). A *gauche* conformation was established in the fragment N–CH_2–CH_2–O and a *gauche-gauche* conformation in N–CH_2–CH_2–CH_2–O. The axis of the unshared electron pair of the nitrogen atom and the line of the O–H bond were disposed in one plane.

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