^{13}C AND ^{1}H NMR SPECTRA OF SPIROPIPERIDINE ALKALOIDS OF Nitraria

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A detailed interpretation is given of the ^{13}C and ^{1}H NMR spectroscopy of the spiropiperidine alkaloids of the nitramine group, and the results are generalized. The assignment has been made of the carbon-13 resonance lines in the spectra of five natural compounds. A dependence of the parameters on the spatial structures of the compounds of this series has been found. The overall PMR spectra of seven natural alkaloids and some of their derivatives are discussed. The conformations of acyl derivatives have been established.

The aim of the present work was to generalize information on the ^{1}H and ^{13}C NMR spectroscopy of spiropiperidine alkaloids of the nitramine group isolated from two species of plants of the genus Nitraria—N. schoberi L. and N. sibirica Pall.

^{13}C NMR Spectra. In papers devoted to a proof of the structures of the compounds discussed below, assignments were made of only some of the signals, mainly those of the methine and quaternary atoms, which were unambiguous. However, the bulk of the peaks due to the carbon atoms of methylene groups remained unidentified. We give a complete assignment of the carbon-13 signals in the NMR spectra of five alkaloids of the nitramine group. For this

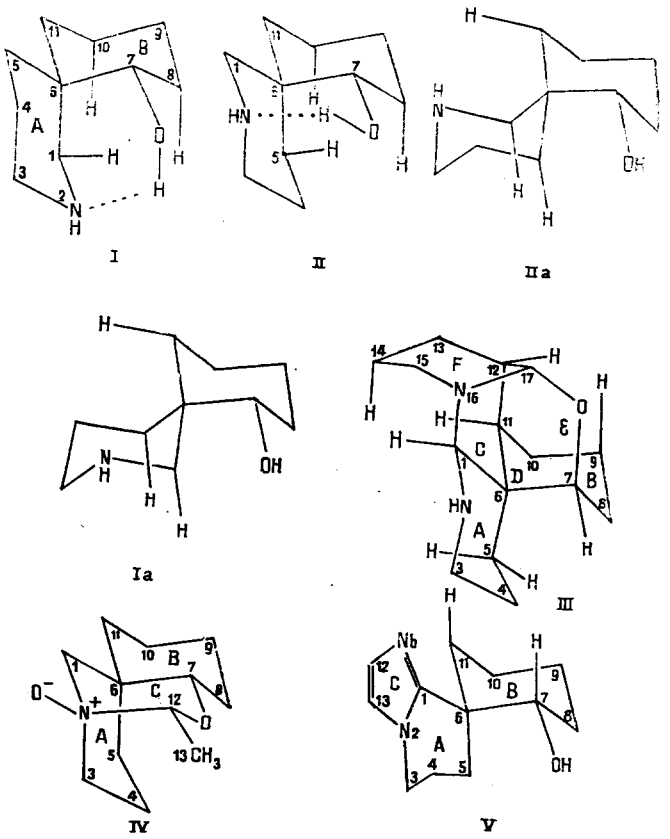

Fig. 1. Structural formulas of alkaloids of the nitramine group.

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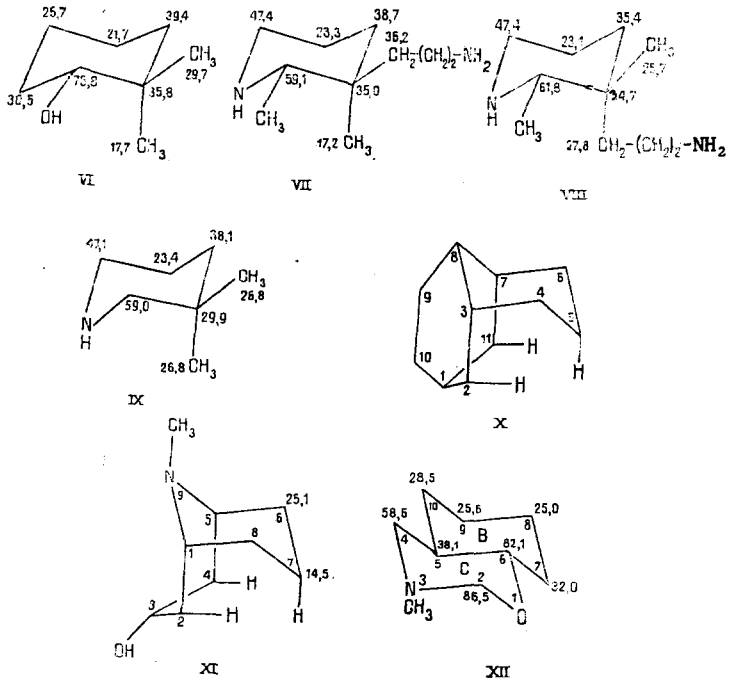

Fig. 2. Structural formulas of model compounds.

purpose we have used information on the multiplet nature of the signals in the spectra with incomplete suppression of C–H interactions, and also information on model compounds. The assignment is based on the general ideas of the theory of the chemical shift [1, 2].

Table 1 gives the values of the chemical shifts (CSs) of the alkaloids nitramine (I), isonitramine (II), nitraramine (III), sibirinine (IV), and nitrabirine (V), and also the increments relative to isonitramine. Figure 1 gives the structural formulas of these alkaloids. Figure 2 illustrates the structural formulas of the model compounds used for comparison, with statements of the CSs of the atoms of interest relative to TMS in $CDCl_3$, with the exception of (VI), the spectrum of which was obtained by the authors in $CFCl_3$ (see the corresponding references).

The first representatives of the group of alkaloids under consideration are the two diastereomeric bases (I) and (II) [3, 4], which are based on the 2-azaspiro[5.5]undecane

TABLE 1. Carbon-13 Chemical Shifts in the Spectra of Alkaloids of the Nitramine Group and Changes in the CSs of the C(1)-C(11) Relative to the Characteristics of Isonitramine (ppm, 0 – TMS; solvent – $CDCl_3$)

Carbon Atom	II [3]	I [3]	Δδ	III [16]*	Δδ	IV [23]	Δδ	V [28]	Δδ
1	60,3	52,0	−8,3	66,4	6,1	77,1	16,8	150,9	90,6
3	47,3	46,7	−0,6	45,3	−2,0	62,0	14,7	44,7	−2,6
4	23,1	23,2	0,1	24,0	0,9	19,0	−4,1	19,7	−3,4
5	28,7	37,4	8,7	21,9	−6,8	26,1[c]	−2,6	21,6	−7,1
6	36,2	36,1	−0,1	32,3	−3,9	38,1	1,9	42,7	6,5
7	79,8	77,0	−2,8	75,9	−3,9	84,3	4,5	74,7	−5,1
8	29,8	32,0	2,2	30,5	0,7	26,8[c]	−3,0	29,1	−0,7
9	24,3	23,9	−0,4	14,5[a]	−9,8	24,6	0,3	24,6	0,3
10	20,4	21,1	0,7	25,1	4,7	21,0	0,6	20,8	0,4
11	36,3	36,3	0,0	37,9[b]	1,6	34,5	−1,8	35,4	−0,9
12	—	—	—	38,8[b]	—	101,9	—	127,7	—
13	—	—	—	28,4	—	14,4	—	117,9	—

*Chemical shifts of the atoms in (III): C(14) – 15.3; C(15) – 50.4; C(17) – 82.2. The mutual exchange of the assignment of the signals denoted by the same letters (a, b, c) is possible.

system. A comparison of the CSs of (I) and (II) (see Table 1) shows that there are differences for C-1, C-5, C-7, C-8, and C-10 and for the first two atoms the value of $\Delta\delta$ is considerable (~8.5 ppm). To explain the reasons of the observed shifts we must consider the geometry of the molecules of (I) and (II).

In (I), the C(6)-C(1) bond is axial and the C(6)-C(5) bond is equatorial to the homocycle B. In (II), which is a conformer with respect to the piperidine ring A, a spiroisomer of nitramine, the situation is the opposite. The stereochemistries of the other bonds in (I) and (II) are the same: C(6)-C(7) are axial and C(6)-C(11) equatorial to ring A; the hydroxy group has the equatorial orientation (see Fig. 1). Thus, the axial protons H-8 and H-10 are in gauche relationship in (I) to H_{eq}-1 and in (II) to H_{eq}-5. Grant and Cheney [5] have shown that because of the polarization of the CH bond of the γ-syn-oriented atom, the nucleus of the eclipsed carbon atom is screened (by approximately 5 ppm) while the proton attached to it is descreened [5]. In 2,2-dimethylcyclohexanol [6] (VI) (Fig. 2), for example, the γ-syn effect of the axial methyl group amounts to 4.1 ppm for C-4 and to 5.0 ppm for C-6 in relation to the corresponding atoms in trans-2-methylcyclohexanol [7].

Zimmerman, et al. have reported that, in spiro compounds, because of the fixing of the atoms in the gauche relationship, the γ-axial effect is approximately 1 ppm greater than in the corresponding gem-dimethyl derivatives [8]. It follows from this that the CSs of C-8 and C-10 in (II) practically coincide with the calculated figures. Some descreening of these atoms in (I) ($\Delta\delta$ 2.2 and 0.7 ppm, respectively; see Table 1) is apparently due to the δ-effect of the nitrogen atom [9].

The CSs of C-11 in (I) and (II) are 3.1 ppm smaller than the CS of C-3 in (VI) because of the γ-anti effect of the nitrogen atom [10]. A confirmation of what has been said is the CS of equatorial methylene group in cis-3-(γ-aminopropyl)-2,3-dimethylpiperidine [11] (VII) (see Fig. 2). A comparison of the CS values of the piperidine moieties of the (I) and (II) molecules (see Table 1) with those of (VII), (VIII) [11], and (IX) [12] (see Fig. 2) shows that they practically coincide, with the exception of one atom in the α-position to the spiro center, which is eclipsed by the C-8 and C-10 methylene groups. For (I), this is the C-1 atom ($\Delta\delta$ 8.3 ppm), and for (II) the C-5 atom ($\Delta\delta$ 8.7 ppm; see Table 1).

The value of the diamagnetic shift agrees well with the figures for C-2 ($\Delta\delta$ 8.6 ppm) and C-3 ($\Delta\delta$ 8.2 ppm), which experience a similar interaction in the spectra of the isomers of cis-decahydroquinoline [13]. The fact that the CS values for C-5 in (I) and C-1 in (II) are close or coincide with those for C-4 and C-2, respectively, in the compounds (VII-IX) confirms the conformations of (I) and (II) established previously from their IR spectra. In the alternative conformations (Ia) and (IIa), additional screening of C-1, C-5, and C-11 through the syn-clinal position of the corresponding protons with respect to heteroatoms should be expected (see Fig. 1). Finally, it must be mentioned that the paramagnetic δ-syn effect of the oxygen atom [9] on C-4 in (I) and (II) [compare with the CSs of the C-5 atom in compounds (VII-IX), Fig. 2] is very slight and is possibly compensated by a diagmagnetic γ-effect of the spiro substitution [8]. Worthy of note is the agreement of the sums of the CSs of all the carbon atoms in nitramine (385.7 ppm) and in its diastereometer nitramine (385.9 ppm), which apparently confirms the existence of both compounds in chloroform solutions in the analogous conformations (I) and (II) with intramolecular hydrogen bonds (and with the smallest number of spatial effects).

On passing to a discussion of the carbon atoms of the other three alkaloids of the nitramine group, it must be mentioned that they all have the isonitramine configuration of the 2-azaspiro[5.5]undecane system (rings A and B). The identification of the signals of the spiro atom C-6 and of the methine carbon atoms C-1, C-7, and C-17, and also of the pair C-11 and C-12, from their multiplet natures in the off-resonance spectrum and in light of the paramagnetic α-shifts of the heteroatoms in the structure of (III) (see Table 1 and Fig. 1) presents no difficulties. In particular, the CS value of C-17 correlate well with the values for C-2 of 1,3-oxazine derivatives [14].

In (III) there are two bicyclononane systems [15] fixed in the chair-boat conformation: rings B/E and C/F [16] (see Fig. 1). For this type of structure the CS of the C-3 atom (7) (numbering of bicyclo]3.3.1]nonane) falls in comparison with the double-chair conformation because of gauche-axial spatial interactions. Thus, in the spectrum of 4-homoisotwistane [(X), Fig. 2] the signal from C-5 resonates at 15.2 ppm [17]. In α-granatonol [(XI), Fig. 2], which exists predominantly in the chair-boat conformation, the CS of the similar C-7

TABLE 2. Parameters of the PMR Spectra of Alkaloids of the Nitramine Group and Some of Their Derivatives (CS, ppm, relative to HMDS; δ scale; splitting constants, J, Hz, solvent – deuterochloroform)

Proton	I [3]	II [3]	III* [16a]	IV [23]	V [28]	XIII	XV [33]	XVI [36]	XVII [16a]	XVIII [16a]
H_{ax}-1	2,37 d** ^2J=11,9	2,44 ^2J=−11,4	3,28 s	3,31 d ^2J=−12,0	—	2,94 d ^2J=−11,5	1,87 d ^2J=−11,5	2,87 s	4,07 br.s	3,08—2,30
H_{eq}-1	3,34 d ^2J=−11,9	2,88 d ^2J=−11,4	—	3,17 dt ^2J=−12,0 ^4J=2,3; 2,3	—	3,68 d ^2J=−11,5	2,51 dt ^2J=−11,7 ^4J=1,6; 1,6	—	—	3,08—2,30
H_{ax}-3	2,58 td ^2J=11,4 ^3J=11,4; 3,3	2,54 td ^2J=−11,4 ^3J=11,4; 3,5	2,64 td ^2J=^3J=12,0	3,70 m	3,91 m	3,40—3,80	1,96 td ^2J=−12,0 ^3J=12,0 3,2	2,55 m	3,02—2,60	,08 — 2,30
H_{eq}-3	2,95 m	2,92 m	3,03 m ^2J=12,0	3,70 m	3,91 m	3,40—3,80	2,73 m	3,20 m ^2J=−12,0	4,80 m ^2J=−12,5	3,08—2,30
H_{eq}-5	2,1—0,9	2,14 m ^2J=−12,5	2,13 m ^2J=−12,0				2,13 m		2,17 m ^2J=−12,0	
H-7	3,48 dd ^2J=9,1; 4,2	3,57 dd ^3J=11,0; 3,5	4,38 br.s $W_{1/2}$= 6,3	3,58 dd ^3J=11,0; 3,5	4,37 dd ^3J=10,0; 4,5	3,40—3,80	3,54 m ^3J=10,1; 4,0	4,19 m $W_{1/2}$= 7,0	3,94 br.s $W_{1/2}$= 6,5	3,65 br.s $W_{1/2}$= 6,5
	O—H 3,05 br.s	O—H 3,87 br.s	H_{ax}-15 2,64 m ^2J=^3J=12,0	H-12 4,58 qd 1:3:3:1 ^4J=1,2	H-12 6,04 d ^3J=1,0	H-12 4,65 q 1:3:3:1	O—H 4,97 dd	—	H_{ax}-15 2,25—2,60	C(15)H_2 2,30—3,08
	N—H 3,98 br.s	N—H 3,87 br.s	H_{eq}-15 3,3 m ^2J=12,0	H-13 1,65 d ^3J=5,7	H-13 6,73 d ^3J=1,0	H-13 1,56 d	N—CH_3 2,17 s	—	H_{eq}-15 2,60—3,02	N—H 2,22 br.s
	—	—	H-17 4,01 d ^3J=2,5	—	O—H 2,93 br.s	—	—	H-17 4,00 d ^3J=2,5	H-17 4,07 br.s	H-17 4.01 d ^3J = 2.5

*N—H signal in (III): 2.44 br.s.

**Multiplet symbols: s, singlet; br.s., broadened singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; td, triplet of doublets; dd, doublet of doublets; qd, quartet of doublets; m, multiplet.

atom amounts to 14.5 ppm [18]. On this basis, the signals at 15.3 and 14.7 ppm in (III) were assigned to C-9 and C-14 (see Table 1).

In (X), the C-4 and C-6 atoms [17] and in bicyclo[3.3.1]nonane the C-2(6) and C-4(8) atoms resonate in the 32-ppm region (see, for example, [19, 20]). The values in the 9-aza derivatives are close to this [18]. The introduction of an axial substituent into position 9 lowers the CSs of these atoms to 25.1 ppm in the case of (XI) (see Fig. 2) and to 24.6 ppm in the spectrum of 9-hydroxybicyclo[3.3.1]nonane [20]. On this basis, the signal at 25.1 ppm in the spectrum of (III) was assigned to C-10 and that at 30.5 ppm, with allowance for the β-effect of the axial oxygen (see, for example, [21]), to C-8.

The signal from C-5 undergoes a considerable diamagnetic shift (6.8 ppm; Table 1) on passing from (II) to (III). The periplanar and γ-anti effects of a heteroatom have been described in detail in [10]. For the simplest monocycles and, in particular, 5-methylsubstituted dioxanes [10] and 1,3-oxazine [14], the screening effect exceeds 10 ppm. It is true that in large systems it is less appreciable, while in those cases where the heteroatom is a substituent in an adamantane or a bicyclo[2.2.2]octane system the effect becomes the opposite [22]. In hydroxy derivatives of bicyclo[3.3.1]nonane, the γ-anti effect is the greatest (4-6.5 ppm) when the heteroatoms and one of the protons of the γ-carbon are the ends of a plane (H_wO) [19]. There are two such fragments with C-5 in (III) (see Fig. 1): O–C(7)–C(6)–C(5)–H_{ax}(5) and N(16)–C(1)–C(6)–C(5)–H_{eq}(5). Apparently, an analogous effect for the oxygen at C-13 lowers its CS to 28.4 ppm as compared with the expected 30-32 ppm (see above).

In sibirinine [(IV), see Fig. 1] [23], rings B and C are trans-linked, while A and C have the double-chair conformation, as in unsubstituted 3-oxa-1-azabicyclo[3.3.1]nonane [24]. Unfortunately, we do not have available the spectrum of the deoxy derivative of (IV) and can trace the influence of an N-oxide function only indirectly, in comparison with isonitramine (see Table 1). A good model for the study of the B/C moiety is trans-N-methyl-5,6-tetramethylenetetrahydro-1,3-oxazine [25] [(XII); see Fig. 2]. When the β- and γ-effects of C-5 on C-11 and C-8, C-10, respectively, are taken into account, almost complete agreement of the CSs in rings B of (IV) (Table 1) and (XII) (Fig. 2) is observed. Some descreening (Δδ

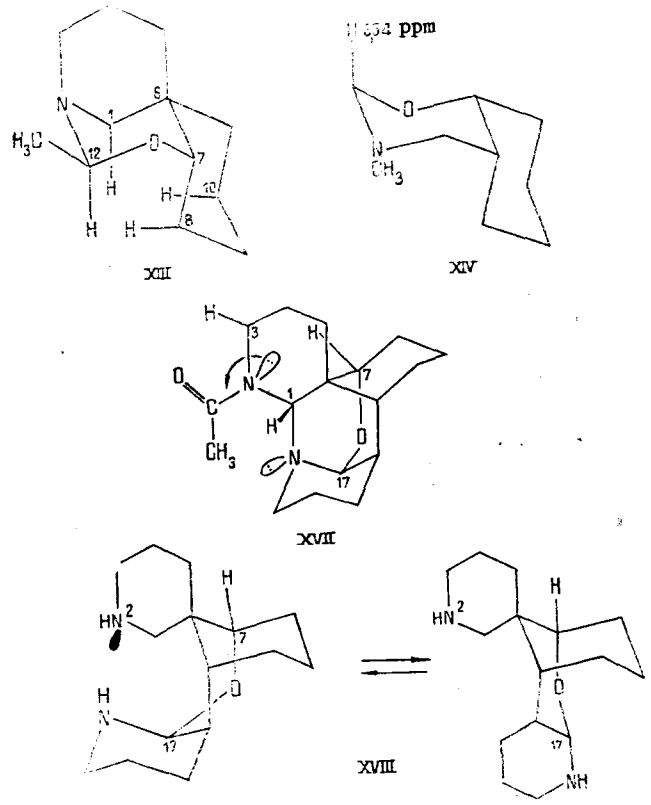

Fig. 3. Some derivatives and analogs of the nitramine group.

2.2 ppm) of C-7 in (IV) is connected either with the β-effect at C-5 or with an electron density distribution as the result of the inductive effect of the positively charged nitrogen atom along the N(2)–C(12)–O–C(7) chain. Strong descreening of C-1, C-3, and C-12 is characteristic for atoms in the α-position to an N-oxide group. As a rule, the β- and γ-effects are diamagnetic [26]. In compounds where the β-atom is tetrasubstituted, a small degree of descreening is observed (for example, in strychnine N-oxide [27]). Identification of the remaining signals was carried out with allowance for these effects and those considered above (see Table 1).

So far as concerns the alkaloid nitrabirine [28] [(V), Fig. 1], in the assignment of the resonance lines in its spectrum we were also guided by the above-stated principles for the identification of the signals (see Table 1). However, the absence of suitable model compounds of the imidazole series does not enable us to speak of the incontrovertibility of the assignment of the signals of the methylene carbon atoms.

As mentioned above, the alkaloids considered, with the exception of nitramine, have the isonitramine configuration of the spiropiperidine moiety A-B (Fig. 1). Therefore, in analysis of the spectra the change in the carbon-13 CS in (III-V) relative to (II) (Table 1) is of definite value, permitting the influence of various steric and electronic effects on the atoms of the common base A-B to be followed. The result of the γ-interactions, both syn-axial [see, for example, Δδ 9.8 ppm for C-9 in (III)] and anti-periplanar [Δδ 6.8 ppm for C-5 in (III)] is particularly appreciable. On the other hand, the increments in the CSs of (I) relative to (II) are due only to the different geometries of the molecules and enable both the diastereomers (I) and (II) and also the conformers (I) and (II) to be distinguished from (Ia) and (IIa) (see Fig. 1).

PMR Spectra. The overall PMR spectra of the alkaloids studied contain less information than the carbon-13 spectra, since the signals of the majority of protons are located in the methylene hump. Table 2 gives the peaks that have been identified in the spectra of the alkaloids of the nitramine group and some of their derivatives. A comparison of the parameters for (I) and (II) shows that only the CSs of the equatorial protons H-1 and H-5 differ appreciably. An analysis of literature information indicates that in piperidine derivatives [11, 29] the α-equatorial protons resonate in the 2.60-3.15 ppm region while the α-axial protons resonate between 2.10 and 2.60 ppm. Consequently, the CS values of the protons at C-1 in the spectrum of (II) and also at C-3 in the spectra of (II) and (I) lie in the usual region. The pronounced descreening of H_{eq}-1 in (I) [Δδ 0.46 relative to (II)] is due to the gauche effect [5] of H_{ax}-8 and H_{ax}-10 [see (I) in Fig. 1]. It must be expected that, as a result of interaction with H_{eq}-1, the latter would resonate in a weaker region of the field than the equatorial protons geminal to them (not differentiated in the 2.00-1.00 ppm region). A similar phenomenon has been described, in particular, for cis-decahydroquinoline [30], the alkaloid luciduline [31], and some spiro compounds [32]. A similar interaction is observed between H_{ax}-8 and H_{ax}-12 in the product of the condensation of (I) with acetaldehyde [see (XIII) in Fig. 3 and Table 2], in the spectrum of which the signal from H_{ax}-12 appears at 4.65 ppm. For comparison, we may mention that H_{ax}-2 in (XII) (see Fig. 2) gives resonance at 4.03 ppm, while that in the cis-isomer (XIV) (Fig. 3) does so at 3.54 ppm [25]. Furthermore, a comparison of the CSs of H_{ax}-2 in (XII) and H_{ax}-12 in (IV) enables the descreening α-effect of the N-oxide function to be evaluated.

As has been shown above, in (II) H_{eq}-5 is in the gauche relationship to H_{ax}-8 and H_{ax}-10, which permits its signal in the spectrum to be observed at the limits of the methylene hump at 2.14 ppm. The multiplet has the form of a doublet with a geminal coupling constant of 12.5 Hz, the components of which are broadened (partially split) through two small vicinial interactions (see Table 2). In the spectrum of sibirine [33] [(XV), antipode of N-methyl-(II)] and of (III), H_{eq}-5 resonates in the region of 2.13 ppm (see Table 2).

In the spectra of (III) and (V) unusually large values of the CS of the H-7 proton are observed. In (V), as in (I) and (II), it has the axial orientation, while in (III) it has the equatorial orientation. In (V), the imidazole ring C and four of the bonds of ring A lie in one plane, and only C-4 deviates from it (see Fig. 1). The mutual positions of the C(7)–H_{ax} bond and ring C are close to planar. Together with the spatial propinquity of the lone pair of electrons (LP) of N_b, these two factors exert a descreening influence H_{ax}-7. In [34], for example, the authors report that the axial carbinol proton of mesembranol, which has a nitrogen atom in the syn-axial position, gives a resonance in a weaker field than the corresponding equatorial proton of epimesembranol.

We observed a similar effect for H-7 in (III). We must mention that there are no direct proofs of the axial orientation of the LP of the N-2 atom in (I), (II), and (III). However, Lambert, et al. [35] consider, on the basis of the results of PMR spectroscopy, that in counterbalance to unsubstituted piperidine, in 3,3-dimethylpiperidine the electron pair of the nitrogen atom is predominantly axial. Noteworthy is the transformation of the H-7 signal on passing from (III) to nitraroxine [(XVI) in Fig. 1; N(2)—OH in (III)] [16a, 36] and to N-acetylnitraramine [(XVII), see Table 2 and Fig. 3], where one must expect a displacement of the LP of N-2 in the direction of the oxygen and the carbonyl carbon, respectively [16a]. In dihydronitraramine [16a] [(XVIII); see Fig. 3 and Table 2], the CS of H-7 has the usual value, which permits us to select the conformation with the maximum distance between the LP of N-2 and H-7. It must be mentioned that the identification of the two weak-field signals in the spectrum of (III) (Table 2) is unreliable, since H-17 gives a clear doublet with a vicinal coupling constant of 2.5 Hz, while its CS (4.01 ppm) lies within the range found for H_{eq}-2 in 1,3-oxazine with the axial orientation of the AEs of the nitrogen atom (3.88-4.21 ppm) [14, 37].

Good information on the structure of N-acetylnitraramine is given by the strong descreening of the equatorial H-3 proton ($\Delta\delta$ 1.77 ppm) and the axial H-1 proton ($\Delta\delta$ 0.79 ppm; see Table 2) in relation to their values in (III). It has been shown [38] that such a situation arises on substituted N-acetylpiperidines for the cis-equatorial and trans-axial α-protons under the conditions of hindered rotation around the amide bond, when it is possible to observe signals for individual rotamers. With free rotation, the descreening magnitudes amount to approximately 1.1 ppm for α-H_{eq} and 0.2 ppm for α-H_{ax} [29, 39]. On this basis, it was concluded that rotamer (XVII) (Fig. 3) with a cis-carbonyl group in relation to the C-3 group predominated. Free rotation was prevented by the LP of the N-16 atom [16a].

In conclusion, we may note that in mono-O-acyl, and also N-substituted O-acyl, derivatives of nitramine and isonitramine inversion of the cyclohexane ring from one chair conformation to another takes place. This follows from the decrease in the half-width of the H-7 signals in the spectra of these compounds (~10 Hz) as compared with that in the initial compound (~20 Hz) and is obviously a consequence of steric interactions.

CONCLUSIONS

A complete assignment of the resonance lines in the ^{13}C NMR spectra of five bases of the nitramine series representing a new class of spiropiperidine alkaloids has been made. A relationship has been found between the chemical shifts of individual atoms and the configuration of conformations of the 2-azaspiro[5.5]undecane system. The magnitudes of the steric and electronic effects playing an important role in the structure of the molecules are discussed. An interpretation is given of the summary PMR spectra of seven natural alkaloids and a number of their derivatives. The conformations of acyl derivatives have been determined on this basis.

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