SPECTROSCOPIC STUDY OF THE LONG-RANGE INTERACTION IN SATURATED HETEROCYCLES

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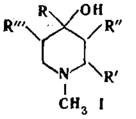
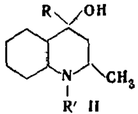
The IR and UV spectra of stereoisomeric piperidines and decahydroquinolines were studied, and it was shown that the spectral characteristics (intensity of the long-wavelength "Bohlman" band of the C−H vibrations, the oscillator strength for the long-wavelength electron transition, etc.) depend on the orientation of the substituents attached to the 2- and 4-ring atoms. The problem of the capacity of the p electrons of nitrogen for partial delocalization owing to the interaction with the anticoplanar α -C−H bonds is discussed.

It was recently [1] demonstrated that for decahydroquinoline derivatives there are rather strict relationships between the orientation of the substituents attached to C_2 and C_4 and the spectroscopic characteristics – the position and intensity of the long-wavelength UV band [2] and the intensity of the so-called "Bohlman" bands in the IR spectrum [3]. A comparison of these results with the data on the basicities of the compounds leads to the conclusion that both the basicity and the spectral characteristics depend to a considerable degree on the relative orientation of the p orbital of nitrogen and the C−H bonds formed by the α-carbon atoms. If they are anticoplanar, the p electrons are appreciably delocalized, and the basicity is reduced as compared with compounds with other relative orientations. The role of a substituent attached to C_4 is not completely clear, although in [4-6] it was shown that the basicity depends not only on the electronegativities of these substituents, but also on their orientations. This fact is not explained by the existing concepts of the inductive effect or successive polarization of the σ bonds induced by an electronegative substituent and diminishing as the distance from it increases [7,8].

It seemed expedient to us to augment the collection of investigated cyclic amines in order to verify the previously drawn conclusions and to attempt to establish the role of the electronegativity and orientation of the C_4 substituent. For this, in this paper we examine the UV and IR spectra of stereoisomeric derivatives of piperidine (I) and 2-methyl-4-hydroxydecahydroquinoline (II).



I



II

IR Spectra. Bohlman [3] demonstrated that the presence of anomalously long-wavelength bands of the valence vibrations of C−H is characteristic for quinolizidine derivatives. It turned out that the constant condition for their appearance is the presence of axial α-hydrogens and an axial p orbital of nitrogen. If the number of α-axial hydrogens is known, the fraction of molecules with an axial orbital can be calculated from the integral intensity of the bands [9,10]

$$\varphi=\frac{S_{B}(N-n)}{S_{CH}\cdot n\cdot K}=\frac{J_{B}}{J_{CH}\cdot K},$$

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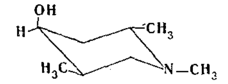
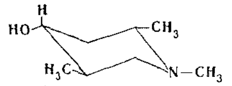
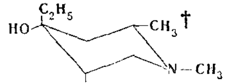
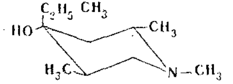
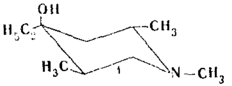
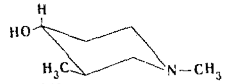
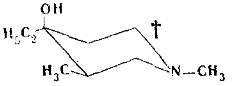
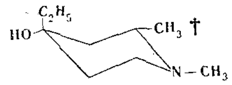
where S_B and S_{CH} are the areas under the "Bohlman" and "normal" C–H bands (in coordinates of D and ν), J_B and J_{CH} are the areas of one "Bohlman" and one "normal" C–H bond, respectively, N is the total number of C–H bonds, n is the number of "Bohlman" C–H bonds, and K is the ratio of the average intensities of the "Bohlman" and "normal" C–H bonds. The K coefficient was determined from the data for 1-methylquinolizidine, in which an axial p orbital is assumed in all of the molecules; it was found to be 1.9 [9]. When the α-carbon is secondary, it is necessary to allow for the fact that both the symmetric and asymmetric vibrations prove to be "Bohlman" vibrations, so that n = 4 for α-unsubstituted compounds, while n = 3 for compounds with one α-substituent, disregarding the contribution from $N-CH_3$. This latter contribution, according to the data in [9], is somewhat less than the contribution of one C–H bond, and, on the basis of a study of $N-CH_3$ derivatives, is estimated to be 3/4 J_B.

From the results presented in Table 1 it is seen that the fraction of molecules with an axial p orbital is high ($\varphi > 50\%$) for all of the compounds, which is characteristic for cyclic tertiary amines [9]. In addition, as a rule, φ is greater for isomers with an equatorial OH group. The same sort of effect was previously detected for piperidine α-derivatives from the results of measurements of the dipole moments [11]. It is important that it is also observed in secondary and tertiary alcohols, and, although it is not expressed

TABLE 1. Spectroscopic Characteristics and Basicities of Substituted Piperidines

Formula	Series	UV spectra							φ, %	pKa in methanol*
		heptane				alcohol		f_{al}/f_h		
		ν_{max}, cm^{-1}	f	$\Delta\nu_{1/2}$, cm^{-1}	f/ν^2	ν_{max}, cm^{-1}	f			
	γ	50100	0,087	5800	34,1	50250	0,008	0,092	55	7,96
	β	49250	0,092	5500	38,1	50250	0,012	0,130	75	7,31
	α	50250	0,092	7100	36,4	50250	0,020	0,220	83	7,83
	β	50000	0,094	6600	37,7	50250	0,015	0,160	72	7,32
	γ	50000	0,094	6600	37,7	50400	0,014	0,150	60	7,82
	α	50000	0,044	6000	17,6	50250	0,004	0,091	62	7,74
	β	49250	0,031	5400	12,8	50250	0,008	0,257	51	7,11
	α	50100	0,045	6800	17,9	50250	0,014	0,312	64	7,70
	β	49250	0,055	6000	22,7	50250	0,020	0,364	65	7,46
	α	—	—	—	—	49800	0,010	—	55	7,98
	β	49250	0,086	5000	35,6	50250	0,023	0,267	74	7,59

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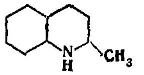
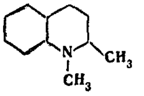
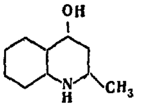
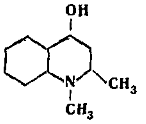
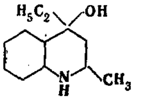
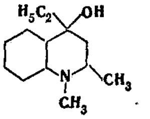
*Data taken from [5].

† The compounds are capable of ring conversion, and the preferred conformation is shown.

TABLE 2. Spectroscopic Characteristics and Basicities of Substituted Decahydroquinolines

Compound	Orientation		UV spectrum		φ, %	pK_a in water*
	CH_3	OH	$\Delta\nu_{1/2}$, cm^{-1}	f/ν^2		
	*a*	—	10000	31,6	—	10,9
	e	—	7000	43,4	—	10,7
	*a*	—	9400	29,5	60	10,6
	e	—	6000	53,4	57	10,4
	*a*	*a*	9400	18,7	8	10,3
	a	*e*	9000	10,3	13	9,9
	e	*a*	6400	20,5	29	10,1
	e	*e*	5400	9,9	31	9,6
	*a*	*a*	8000	25,8	62	9,90
	a	*e*	7600	22,2	59	9,45
	e	*a*	5200	35,8	53	9,63
	e	*e*	4800	37,0	56	9,26
	*a*	*a*	8200	8,8	47	9,24†
	e	*a*	5400	5,3	48	9,01†
	e	*e*	4800	3,5	46	8,53†
	*a*	*a*	6200	17,0	56	—
	e	*a*	4000	23,8	63	—
	e	*e*	5000	20,8	58	—

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*Data taken from [4].

†In methanol.

as strongly as in the case of secondary amines, it is still sufficiently clearly noticeable. The basicity of the amines under consideration changes in opposition to the φ value; isomers with an equatorial hydroxyl group always have lower pK_a values than their axial epimers (see Table 1 and also [5]).

UV Spectra. The long-wave absorption of the amines under consideration is undoubtedly caused by a transition of the p electrons of nitrogen, the contribution of which to the total polarizability is proportional to f_i/α_i^2, where f_i is the oscillator force (calculated as $4.3 \cdot 10^{-9} \cdot \varepsilon_{max} \cdot \Delta\gamma_{1/2}$), and γ_i is the frequency of the corresponding band [1,12]. Two long-wave transitions are possible for aliphatic amines: $n \rightarrow \sigma^*$ (if the n orbital is a pure 2s orbital), and $n \rightarrow 3s$ (if the n orbital is a pure 2p orbital). Their frequencies are close, and, depending on the character of the actually existing hybrid n orbital, redistribution of the intensity between the $n \rightarrow \sigma^*$ and $n \rightarrow 3s$ transitions is possible. When the contributions of the s and p orbitals are close, the two transitions are equally probable, and the corresponding band has the maximum half width for the minimum intensity in the maximum. If, however, one of the transitions predominates, two variants are possible: either the integral intensity remains unchanged, regardless of the transition realized, or it depends on the type of transition and, consequently, the geometry of the molecule. It is seen from Table 1 that in the series of compounds under investigation we are dealing with the latter case. Since the integral intensity determines the contribution of a given transition to the total static polarizability of the molecule, the data obtained indicate the difference in this contribution for the different isomers. The change in the polarizability may be the result of either a change in the ionization potential or a change in the degree of delocalization of the electrons. Since the observed relative changes in the frequency of the band maximum (γ_i) with changing configuration are extremely small in comparison with the change in the oscillator force, the differences in the polarizabilities of the isomers are therefore caused by a change in the degree of delocalization of the electrons. This also means a change in their bonding character and, consequently, the degree of unsaturated character of the isomers.

A more detailed comparison of the data on the polarizability of stereoisomeric molecules with the characteristics of their reactivities is of interest. The basicity may, on the one hand, stand out as a characteristic of this sort, or, on the other hand, the spectroscopic effect of a hydrogen bond (f_{al}/f_h, where f_{al} and f_h are, respectively, the oscillator force for the same molecule in nonsolvating hexane and in the electron-acceptor solvent alcohol, in which the intramolecular tying up of p electrons is replaced by solvation of the O−H...N type) may serve in such a function. This sort of comparison can be carried out most graphically in the case of 4-hydroxydecahydroquinolines with a rigid configuration. It is apparent from the data in Table 2 that there are at least two different types of substituent effects on the basicity and polarizability of a molecule; these two types may be termed "symbatic" and "antibatic" effects. The "symbatic" effect, which is induced by the introduction of an OH group, with an appreciably greater electronegativity than hydrogen, into the 4-position leads to a decrease in both the polarizability and basicity (the form of the band does not change in the process). In this sense, this type of effect can apparently be termed an inductive effect. However, even it does not fit completely into the classical concepts of the inductive effect, since the effect of a hydroxyl group is different in magnitude, depending on its orientation, and an axial hydroxyl group is associated with a higher polarizability and higher basicity.

From the data of Table 1 it can be seen that for piperidine compounds, in all cases, the transition from the isomer with an axial hydroxyl group in the 4-position to the equatorial epimer also leads to a decrease in the basicity (see also [5]) and to a reduction in the spectroscopic effect of a hydrogen bond. As already noted, the fraction of molecules with an axial p orbital also generally increases in the process. Of course, it is true that, in contrast to decahydroquinoline derivatives, the dependence of f_i/γ_i^2 on the molecular geometry is expressed less distinctly in the piperidine series. This is apparently associated with the lower rigidity of the molecules and with their greater tendency for different ring distortions, and, in a number of cases, for conformational transformations (see Table 1).

In contrast to an OH substituent attached to C_4, a methyl substituent attached to C_2 has an "antibatic" effect: the basicity decreases on passing from an axial to an equatorial orientation, while the polarizability increases (see Table 2).* This case is of special interest. An increase in polarizability is usually a consequence of either a decrease in the ionization potential or an increase in the effective electron charge on the nitrogen atom. In any case, this should be accompanied by an increase in the basicity because of a decrease in the difference ($I_{R_3N} - E_{R_3NH^+}$), which determines the energetics of the acid−base reaction. The case in which a decrease in basicity corresponds to an increase in the polarizability can be realized only when the reason for the increase in the polarizability is an increase in the lability of the electrons within the limits of the molecule. It is known [12] that the polarizability and refraction are greater than their sum in those cases in which the molecule contains multiple and, especially, conjugated multiple bonds. In the molecules under consideration, there are formally no unsaturation or conjugation. However, it is clear from the data presented that the p electrons of nitrogen, which determine the reactivity of the amine and are formally atomic, can be delocalized, even if only partially. The observed "antibatic" effect can then be considered to be a confirmation of the conclusion drawn above regarding the change in the bonding character of the p electrons as a function of the molecular configuration. In fact, if the axial α-hydrogen increases the bonding character of the p electrons, thereby giving them a larger space for delocalization, the polarizability should increase in the process, and the capacity for donor−acceptor interaction (characterized by f_{al}/f_h or pK_a) should decrease for compounds with an equatorial CH_3 group as compared with the axial C_2 isomer. The difference in the character of the effects induced by the OH group in the 4-position and the CH_3 group in the 2-position is an important confirmation of the qualitative difference in the essence of the phenomenon that is called the inductive effect for different types of substituents, which was noted in [8].

In a number of features, the observed effect recalls hyperconjugation or the single bond conjugation discussed by Nesmeyanov [14]. According to Nesmeyanov, the effectiveness of the interaction between single bonds in the A−B−C−D system is high when the A−B and C−D bonds are anticoplanar and the corresponding orbitals are situated at different ends of the electronegativity scale (or Lewis acidity scale): one is a donor, and the other is an electron acceptor. In our case, the N−C−H fragment completely satisfies this condition for an axial C−H bond that is an acceptor owing to a high ionization potential and for an axial orientation of a p orbital that acts as a donor. A consequence of this sort of conjugation of the p orbital of nitrogen and the σ orbital of the C−H bond is involvement of the p electrons in bonding with a simultaneous increase in their polarizability as a result of delocalization in a relatively large fragment. The intramo-

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*A similar effect is also observed during replacement of NH by N−CH_3, but in this case the interpretation of the data is difficult, since the decrease in basicity may be associated with the change in the solvation during alkylation of the amines [13].

lecularly tied up p electrons have a lesser tendency for intermolecular interaction, and the reactivity of the molecule is reduced.

Thus the data obtained make it possible to assume that under certain conditions the interaction between saturated bonds ("$\sigma - \sigma$" or "$p - \sigma$ conjugation") may play an extremely important role in the formation of the reactivity of the molecule.

LITERATURE CITED

1. S. S. Chasnikova, V. I. Artyukhin, O. V. Agashkin, G. S. Litvinenko, and D. V. Sokolov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 3, 52 (1968).
2. A. D. Walsh and P. A. Warsop, Trans. Faraday Soc., 57, 345 (1961).
3. F. Bohlman, Ber., 91, 2157 (1958).
4. G. S. Litvinenko, V. I. Artyukhin, A. A. Andrusenko, D. V. Sokolov, and K. I. Khludneva, Reakts. Sposobn. Organ. Soed., 5, 263 (1968).
5. T. D. Sokolova, S. V. Bogatkov, B. V. Unkovskii, E. M. Cherkasova, and Yu. F. Malina, Reakts. Sposobn. Organ. Soed., 5, 160 (1968).
6. É. A. Mistryukov and N. I. Aronova, Izv. Akad. Nauk SSSR, Ser. Khim., 789 (1967).
7. R. A. Bent, Can. J. Chem., 38, 1235 (1960).
8. V. A. Palm, Fundamentals of the Quantitative Theory of Organic Reactions [in Russian], Khimiya, Leningrad (1967).
9. O. V. Agashkin, V. I. Artyukhin, D. V. Sokolov, T. Zhaparov, K. I. Khludneva, and G. S. Litvinenko, Izv. Akad. Nauk Kaz. SSR, Ser. Khim., No. 5, 46 (1969).
10. T. Masamune and M. Takasugi, Chem. Comm., 625 (1967).
11. B. A. Arbuzov, G. G. Butenko, and A. N. Vereshchagin, Dokl. Akad. Nauk SSSR, 172, 1323 (1967).
12. M. V. Vol'kenshtein, Structure and Physical Properties of Molecules [in Russian], Moscow–Leningrad (1955).
13. F. E. Condon, J. Am. Chem. Soc., 87, 4481 (1965)
14. A. N. Nesmeyanov, Uch. Zap. MGU, 132, 5 (1950).