

Organic ammonium salts. II.

Study of the infrared spectra of 1,1-dialkylpiperidinium bromides

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*Dedicated to Professor J. Majer, Corresponding Member of the
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The influence of the length of alkyl chain in 1,1-dialkylpiperidinium bromides on stretching vibrations of the C—H and C—C bonds has been studied. A conception of the spatial arrangement of the alkyl chains bonded to the ammonium nitrogen of the heterocyclic ring was derived on the basis of infrared spectroscopy.

Изучалось влияние длины цепи алкила в 1,1-диалкилпиперидинийбромиде на валентные колебания связей C—H и C—C. На основании ИК спектроскопии высказывается предположение о пространственном расположении алкильных цепочек, присоединенных к аммониевому азоту гетероциклического кольца.

The absorption bands of stretching vibrations of the C—H bonds in six-membered cyclic systems with a minimum strain of the ring appear in the same region as those of alkanes ([1], 145, 125; [2]).

The intensities of the bands of stretching vibrations of the C—H bonds in the $>CH_2$ and $-CH_3$ groups are proportional to the number of the groups present in molecules and for the saturated hydrocarbons they increase with the length of chain [3, 4]. Jones [5] measured the effective values of the absorption coefficients of seventeen non-branched alkanes and found that the molar absorption coefficient increased linearly with the length of chain. The molar absorption coefficients of the bands corresponding to the $-CH_3$ and $-CH_2-$ groups may be quite different when compared with those of the above-mentioned compounds provided that the hydrocarbons contain other elements, especially sulfur and oxygen [6].

The overtones and combination bands of bending vibrations of the C—H bonds in the $-CH_3$ and $>CH_2$ groups become intense owing to the Fermi resonance and appear also in the region of stretching vibrations of the C—H bond. But they occur

at lower wavenumbers than the major bands of C—H bonds corresponding to stretching vibrations. An exactly resolved band can be seen with the derivatives of cyclohexane at $\sim 2700\text{ cm}^{-1}$ [7]. These bands are used for the stereochemical study of the piperidine derivatives and were first reported by *Bohlmann* [8] who found an empirical relationship between the configuration of the quinolizidine derivatives and their infrared bands in the region $2800\text{—}2700\text{ cm}^{-1}$. *Tsuda* [9] used the Bohlmann criteria for partially deuterated piperidines. His results confirm the finding on a preponderantly axial orientation of the lone electron pair reported in [10—12]. *Hamlow et al.* [13] have explained the differences in the bands reported by Bohlmann as well as in the chemical shifts (0.80—0.93 p.p.m.) of axial and equatorial α protons which are due to the overlap of the lone electron pair of the antibonding σ^* C—H_{axial} orbital on the adjacent carbon.

Brown et al. [14] investigated the course of quaternization of 1-alkylpiperidines by means of i.r. and $^1\text{H-NMR}$ spectroscopy. The authors confirmed that the axial attack was favoured in the majority of the investigated reactions.

For ammonium compounds it is not possible to observe separately stretching vibrations in the $\text{=N}^{\oplus}\text{—CH}_2\text{—}$ or $\text{=N}^{\oplus}\text{—CH}_3$ groups (in contrast to secondary and tertiary amines) because of the formation of a positive charge on the nitrogen atom [7]. It follows from this fact that for ammonium salts all kinds of stretching vibrations of the $\text{—CH}_2\text{—}$ groups both in the piperidine ring and the alkyl chains bonded to the nitrogen atom of piperidine can be observed at equal wavenumbers.

Experimental

The infrared spectra of the investigated compounds were recorded on double-beam spectrophotometers (Zeiss, Jena): a) UR-10 (in the region from 3100 to 2800 cm^{-1}) with LiF cells (0.028 or 0.039 mm) at the recording speed of $32\text{ cm}^{-1}\text{ min}^{-1}$; b) UR-20 (in the region from 4000 to 670 cm^{-1}) with NaCl cells (0.110 mm) at the recording speed of $64\text{ cm}^{-1}\text{ min}^{-1}$.

The wavenumber was calibrated by means of polystyrene foil. The accuracy of wavenumber reading varied in the range $\pm 1\text{ cm}^{-1}$. In both cases chloroform of anal. grade was used as a solvent (before use it was deprived of alcohol and moisture by passing through a column packed with silica gel).

1-Alkyl-1-ethylpiperidinium bromides listed in Table 2 were prepared according to [15] and measured at the 0.15 M concentration. The effective values of the molar absorption coefficients ϵ^a were calculated from the absorbance measured by compensation method using the average values of three measurements (see conditions sub a)).

The infrared spectrum of compound *XIII* was recorded by the KBr technique by preparing a paste of this substance in hexachloro-1,3-butadiene (by rubbing the ammonium salt in a mortar). In order to compare the spectra of the ammonium salts with the spectrum of tertiary amine we recorded the spectrum of 1-dodecylpiperidine in original state in the form of a film on a NaCl window as well as in chloroform solution.

Results and discussion

The general valuation of the spectra (region from 4000 to 670 cm^{-1}) showed certain changes due to the state of aggregation of the compounds studied.

a) The infrared spectra taken in *chloroform solutions* exhibited very intense bands in the region of stretching vibrations (2960—2855 cm^{-1}) of the C—H bond. The bands corresponding to asymmetric bending vibrations of the C—H bonds ($\delta_{\text{as}}(\text{CH}_2) + \delta_{\text{as}}(\text{CH}_3)$ of the "scissoring" type) were of medium intensity in the interval from 1480 to 1465 cm^{-1} as well as the skeletal vibrations of the C—C bond in the range from 1250 to 1230 cm^{-1} . Only a weak absorption doublet band was to be observed in the region from 1400 to 1370 cm^{-1} (symmetric bending vibrations of the C—H bonds) except the spectrum of compound *I* ($\delta_{\text{s}}(\text{CH}_3)$ of the "scissoring" type). In contrast to the above-mentioned asymmetric vibrations these vibrations appeared in a clearly resolved doublet band only in the case of compounds *III—VIII*.

b) The infrared spectra recorded by the *KBr technique* differed from the spectra measured in chloroform solutions mainly by a conspicuous absorption band at 722 cm^{-1} (it did not appear in chloroform because of a great absorption of solvent in this region) which was due to the bending vibrations of the "rocking" type ($\rho(\text{C—H})$) ([1], 125). The absorption band of the skeletal vibration appeared at 1215 cm^{-1} as a band of weak intensity (compound *XIII*). The bands of symmetric bending vibrations of the C—H bonds appear in spectra as doublets which are shifted to higher wavenumbers (1415—1395 cm^{-1}) if the band at 1375 cm^{-1} is present.

c) For compound *XIII* the absorption region of the C—H vibrations was also investigated in *hexachloro-1,3-butadiene*. Besides the above-mentioned intense bands we also located weak absorption bands at 2735 and 2660 cm^{-1} which did not appear in solution (at 0.15 M concentration and with the 0.110 mm cell). According to Bohlmann these bands were also present in the spectrum of tertiary amine

Table 1

Some characteristic absorption bands of 1-dodecylpiperidine (*A*) and 1-dodecyl-1-ethylpiperidinium bromide (*XII*) in chloroform solutions

Compound	$\nu_{\text{as}}(\text{CH}_2)$	$\nu_{\text{s}}(\text{CH}_3)$	$\nu_{\text{s}}(\text{CH}_2)$	$\nu(\text{N—CH}_2)$	ν (bands according to [8])	
<i>A</i>	2929	2873	2856	2810	2745 sh	2695
				2773		2670
<i>XII</i>	2930	2875	2857	—	—	—

sh — shoulder of the stronger absorption band (at 2670 cm^{-1}).

(1-dodecylpiperidine) measured in the liquid state as a film between the NaCl windows and in chloroform solution (0.15 M concentration, 2.26 mm NaCl cell). The spectra of tertiary amine and of the corresponding ammonium salt *XII* in CHCl_3 solutions in the region of the stretching C—H vibrations are compared in Table 1. We used the absorption bands of stretching vibrations of the $>\text{N}-\text{CH}_2$ bond as an analytical proof of the presence of tertiary amine during the preparation of the ammonium salt which lacks this band.

Besides the Bohlmann bands we also revealed the bands in the region $900-840\text{ cm}^{-1}$ which were analytical according to the empirical rule proposed by *Brown et al.* [14]. In this region the investigated 1-dodecylpiperidine exhibits only one fairly conspicuous absorption band at 863 cm^{-1} both in chloroform solution and in the liquid state. According to *Brown et al.* [14], the corresponding ammonium compound (1-dodecyl-1-ethylpiperidinium bromide *XII*) shows one band at 882 cm^{-1} .

The main aim of our study of the infrared spectra was to investigate the influence of the length of alkyl chain bonded to the ammonium nitrogen on stretching vibrations of the C—H bond. The results are summarized in Table 2 and shown in Fig. 1. It ensues from the values of the measured effective molar absorption coefficients that the intensities of the absorption bands which correspond to stretching vibrations of the $-\text{CH}_2-$ groups increase proportionally with the length

Table 2

Absorption bands (in cm^{-1}) of the C—H bonds in 1-alkyl-1-ethylpiperidinium bromides

Compound	Alkyl	$\nu_{\text{as}}(\text{CH}_2)$	$\nu_{\text{s}}(\text{CH}_2)$	$\nu_{\text{s}}(\text{CH}_3)$
<i>I</i>	Methyl	2944		
<i>II</i>	Ethyl	2943		
<i>III</i>	Propyl	2943		
<i>IV</i>	Butyl	2942		2880
<i>V</i>	Pentyl	2941		2877
<i>VI</i>	Hexyl	2938	2865	2877
<i>VII</i>	Heptyl	2934	2863	2876
<i>VIII</i>	Octyl	2933	2861	2875
<i>IX</i>	Nonyl	2934	2860	2876
<i>X</i>	Decyl	2933	2859	2874
<i>XI</i>	Undecyl	2932	2859	2874
<i>XII</i>	Dodecyl	2930	2857	2874
<i>XIII</i>	Tridecyl	2930	2857	2874
<i>XIV</i>	Tetradecyl	2929	2857	2874
<i>XV</i>	Pentadecyl	2930	2857	2874
<i>XVI</i>	Hexadecyl	2929	2857	2874
<i>XVII</i>	Octadecyl	2929	2854	2873

of alkyl chain in the case of symmetric and asymmetric vibrations. However, this length has little influence on the intensity of symmetric vibration of the methyl groups the number of which is constant. The increase of the effective molar absorption coefficients is not exactly linear in the whole interval as it is for non-branched alkanes (Fig. 1). At the beginning, the increase of molar absorption coefficients is smaller for alkyl chains with the number of the $-\text{CH}_2-$ groups from 1 to 9. The position of absorption maxima with respect to the increase of the effective values of molar absorption coefficients slightly shifts to lower values of wavenumbers not only for stretching vibrations of the $-\text{CH}_2-$ groups but also of the $-\text{CH}_3$ groups. The difference between the wavenumbers is as follows:

$$\nu_{\text{as}}(\text{CH}_2) - \Delta\bar{\nu} = -15 \text{ cm}^{-1}$$

(number of the $-\text{CH}_2-$ groups = 1–18),

$$\nu_{\text{s}}(\text{CH}_2) - \Delta\bar{\nu} = -11 \text{ cm}^{-1}$$

(number of the $-\text{CH}_2-$ groups = 6–18),

$$\nu_{\text{s}}(\text{CH}_3) - \Delta\bar{\nu} = -7 \text{ cm}^{-1}$$

(number of the $-\text{CH}_2-$ groups = 4–18).

We also observed that the wavenumber of the skeletal C—C vibrations decreased with the length of alkyl chain (the values are not given in Table 2). As

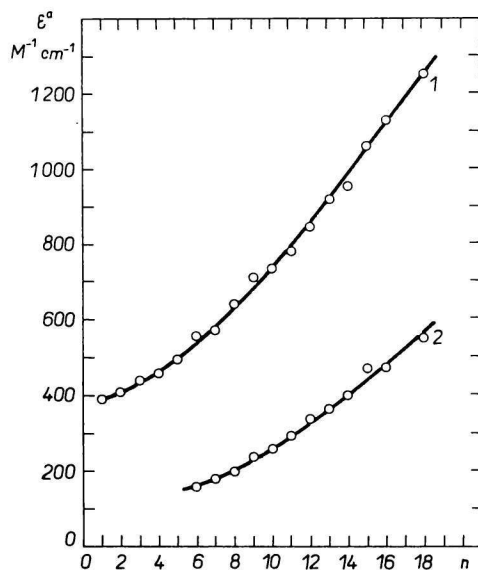


Fig. 1. Dependence of the effective values of molar absorption coefficient ϵ^0 on the length of alkyl chain (n = number of carbon atoms in the chain).

1. $\nu_{\text{as}}(\text{CH}_2)$; 2. $\nu_{\text{s}}(\text{CH}_2)$.

the absorption band corresponding to symmetric stretching vibrations of the $-\text{CH}_3$ groups was approximately of a constant intensity which was relatively low when compared with that of the band of the $-\text{CH}_2-$ groups, only the positions of this band are presented in Table 2. The absorption corresponding to asymmetric vibrations of the $-\text{CH}_3$ groups was covered in the spectra by the stronger band of the $-\text{CH}_2-$ groups and was merely to be located by the point of inflexion on the arm of the band ($\nu_{\text{as}}(\text{CH}_2)$) in the region 2960 cm^{-1} .

From the decrease in wavenumber of the bands of the $-\text{CH}_2-$ groups with their number in chain on the ammonium nitrogen as well as from the decrease in skeletal vibrations it may be concluded that energetically more favourable spatial configurations arise. Presumably, the alkyl chain possesses the form of a helix which rotates around the piperidine ring. That may be explained by a high electronegativity of the positively charged ammonium nitrogen, *i.e.* by a different electron potential between the σ bonds of the aliphatic chain and a positive charge of the ammonium nitrogen. This phenomenon starts to manifest itself from the alkyl chain with six carbon atoms upwards as a change in $\nu_{\text{as}}(\text{CH}_2)$. A comparison of the value corresponding to a short chain (CH_3 , $\nu_{\text{as}}(\text{CH}_2) = 2944\text{ cm}^{-1}$) with the value corresponding to the derivative with six carbon atoms in the chain ($\nu_{\text{as}}(\text{CH}_2) = 2938\text{ cm}^{-1}$) shows that the change is equal to 6 cm^{-1} . With the number of carbon atoms in the chain ranging from 8 to 18, such an outstanding difference was not observed ($\nu_{\text{as}}(\text{CH}_2) = 2933\text{ cm}^{-1}$ for $C = 8$ and $\nu_{\text{as}}(\text{CH}_2) = 2929\text{ cm}^{-1}$ for $C = 18$). On the basis of the course of quaternization described by *Brown et al.* [14] we assume a preferential equatorial orientation of the shorter alkyl chain and an axial orientation of the longer chain for the ammonium salts investigated.

References

1. Rao, C. N. R., *Chemical Applications of Infrared Spectroscopy*. Academic Press, New York, 1963.
2. Fox, J. J. and Martin, A. E., *Proc. Roy. Soc. A* **175**, 208, 234 (1940).
3. Francis, S. A., *J. Chem. Phys.* **18**, 861 (1950).
4. McMurry, H. L. and Thornton, V., *Anal. Chem.* **24**, 318 (1952).
5. Jones, R. N., *Spectrochim. Acta* **9**, 235 (1957).
6. Pozefsky, A. and Coggeshall, N. D., *Anal. Chem.* **23**, 1611 (1951).
7. Colthup, N. B., Daly, L. H., and Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, p. 198. Academic Press, New York, 1964.
8. Bohlmann, F., *Chem. Ber.* **91**, 2157 (1958).
9. Tsuda, M. and Kawazoe, Y., *Chem. Pharm. Bull.* (Tokio) **16**, 702 (1968).
10. Baldock, R. W. and Katritzky, A. R., *J. Chem. Soc. (B)* **1968**, 1470.
11. Baldock, R. W. and Katritzky, A. R., *Tetrahedron Lett.* **1968**, 1159.
12. Masamune, T., Takasugi, M., and Matsuki, M., *Bull. Chem. Soc. Jap.* **41**, 2466 (1968).
13. Hamlow, H. P., Okuda, S., and Nakagawa, N., *Tetrahedron Lett.* **1964**, 2553.
14. Brown, D. R., Lygo, R., McKenna, J., and McKenna, J. M., *J. Chem. Soc. (B)* **1967**, 1184.
15. Lacko, I., Devínsky, F., Mlynářčík, D., and Krasnec, L., *Česk. Farm.*, in press.

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