

Organic ammonium salts. VII.*

Preparation and infrared spectra of some ammonium derivatives of 11-aminoundecanoic acid

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Received 13 February 1979

The preparation and i.r. spectra of some derivatives of 11-aminoundecanoic acid, namely betaines of alkyl(10-carboxydecyl)dimethylammonium bromides and some esters of dodecyl(10-alkoxycarbonyldecyl)dimethylammonium bromides, are described.

Описан синтез и ИК спектры некоторых производных 11-аминоундекановой кислоты, в частности бетаинов бромистого алкил(10-карбокситецил)диметиламмония и некоторых эфиров бромистого додецил(10-алкоксикарбонилдецил)диметиламмония.

When studying some organic ammonium salts as potential solubilizers [1—4] we found that they possessed good surface-active properties as well as significant antimicrobial activity. The assumption of favourable relationship between the effect of the ammonium group and the properties of the alkanecarboxylic acid and of its esters, respectively, prompted us to prepare the title compounds and study their properties. The structures of the prepared compounds were determined mainly by i.r. spectroscopy similarly as in [5].

Experimental

The conditions of measurements of the i.r. spectra and the type of instrument are presented in each table. The spectra were measured in the region of 4000—400 and 4000—600 cm^{-1} , respectively. The apparatus was calibrated with polystyrene foil; the reading accuracy was $\pm 1 \text{ cm}^{-1}$. The effective molar absorption coefficients ϵ^* and the half-widths of bands $\Delta\nu_{1/2}$ were calculated from the absorbance measured by compensation method. The results are presented in Tables 3—6.

* Part VI: Lacko, I., Devínsky, F., Mlynarčík, D., and Krasnec, L., *Z. Naturforsch.* C34, 485 (1979).

$^1\text{H-N.m.r.}$ spectra were measured in CDCl_3 on a Tesla BS 487 A apparatus (80 MHz) at laboratory temperature using tetramethylsilane as internal standard; concentration 10%.

The Raman spectra were measured on a JRS-S 1, Jeol instrument in the region of $0\text{--}4000\text{ cm}^{-1}$; laser Ar^+ 489 nm, slit $6.8\text{ cm}^{-1} \times 10\text{ mm}$, chart speed $0.5 \times 100\text{ cm}^{-1}\text{ min}^{-1}$.

The molecular weights were determined in chloroform on a Dampdruck Osmometer, Knauer (Table 1).

For measuring the dissociation constants ($\text{p}K_a$) on a pH M-26 Radiometer with glass and calomel electrodes, methanolic solutions (40 ml) of betaines (concentration 10^{-3} M) were titrated with 0.1 M-KOH (in 90% methanol) at 20°C . The potential of the electrode was standardized in methanol for 15 min. The activity of H^{\oplus} ions served as starting data for calculations; the results are presented in Table 1.

The purity of all compounds was checked by t.l.c. (R_f =the average value of 8 measurements) on Silufol[®] in the system of acetone-1 M-HCl (1:1); detection with Munièr's modification of the Dragendorf reagent [6].

Ammonium salts

Method A

11-Bromoundecanoic acid [7] (0.1 mol), alkyldimethylamine [8] (0.11 mol), and dry methyl cyanide (25 ml) were heated under reflux for 4-6 h. After cooling the solvent was distilled off and the product was purified by manifold crystallization from dry acetone. Nonhygroscopic white powdery compounds, little soluble in water, insoluble in ether, petroleum ether, soluble in ethanol and chloroform, were obtained. Their characterization is in Table 1.

Didodecyldimethylammonium bromide (DMABr) was prepared from dodecyl-dimethylamine and 1-bromododecane. Yield: 86%; m.p. $172\text{--}175^\circ\text{C}$; $R_f = 0.54$.

Method B

Ester of 11-bromoundecanoic acid [9, 10] (0.05 mol), dodecyldimethylamine (0.05 mol), and dry methyl cyanide (20 ml) were heated under reflux for 6 h. After cooling, the unreacted and decomposition products were extracted into petroleum ether. Methyl cyanide solution was separated, the solvent was distilled off and the extremely hygroscopic products were dried in a vacuum dessicator over P_4O_{10} at 2.7 Pa and laboratory temperature. The products X-XV were oils, the others were solid compounds. Their characterization is in Table 2. All compounds prepared in this manner were well soluble in water, ether, acetone, chloroform, ethanol, benzene and insoluble in petroleum ether.

Results and discussion

The paper deals with the preparation and i.r. spectra of organic ammonium salts derived from 11-aminoundecanoic acid (Table 1) and its esters, respectively (Table 2) as potential solubilizers and antimicrobially active compounds. The activity of these compounds is dealt with in [11]. The ammonium salts of esters

Table 1
 Characterization of alkyl(10-carboxydecyl)dimethylammonium bromides
 $R(CH_3)_2N^{\oplus}(CH_2)_{10}COO^{\ominus}HBr$

Compound	R	Formula	M	Calculated/found			Yield %	M.p. °C	R _f	pK _a
				% C	% H	% N				
I	Butyl	C ₁₇ H ₃₆ BrNO ₂	366.35	55.13	9.90	3.82	83	81—82	0.78	6.91
				55.37	10.13	3.68				
II	Hexyl	C ₁₉ H ₄₀ BrNO ₂	394.40*	57.86	10.22	3.55	80	76—78	0.75	7.04
				57.99	10.38	3.55				
III	Octyl	C ₂₁ H ₄₄ BrNO ₂	422.46	59.70	10.49	3.30	89	87—88	0.63	6.91
				60.02	10.78	3.02				
IV	Decyl	C ₂₃ H ₄₈ BrNO ₂	450.51	61.31	10.74	3.11	87	89—90	0.59	6.93
				61.55	11.03	3.00				
V	Dodecyl	C ₂₅ H ₅₂ BrNO ₂	478.56*	62.74	10.95	2.93	89	91—93	0.47	7.10
				62.60	11.03	3.03				
VI	Tetradecyl	C ₂₇ H ₅₆ BrNO ₂	506.62	64.01	11.15	2.77	85	94—96	0.36	7.05
				63.85	11.00	2.88				
VII	Hexadecyl	C ₂₉ H ₆₀ BrNO ₂	534.67	65.14	11.32	2.62	84	109—111	0.28	7.08
				64.70	11.38	2.32				
VIII	Octadecyl	C ₃₁ H ₆₄ BrNO ₂	562.72*	66.11	11.46	2.48	85	102—103	0.19	7.11
				66.26	11.51	2.34				

* Molecular weight determined: II — 393.6; V — 479.1; VIII — 563.4.

Table 2
 Characterization of dodecyl(10-alkoxycarbonyldecyl)dimethylammonium bromides
 $C_{12}H_{25}(CH_3)_2N^{\oplus}(CH_2)_{10}COOR Br^{\ominus}$

Compound	R	Formula	M	Calculated/found			Yield %	M. p. °C	R _f
				% C	% H	% N			
IX	Methyl	C ₂₆ H ₅₄ BrNO ₂	492.62	63.39	11.05	2.84	80	41—43 Capillary tube	0.54
				63.49	11.25	2.72			
X	Ethyl	C ₂₇ H ₅₆ BrNO ₂	506.64	64.00	11.14	2.76	86	—	0.53
				63.90	11.35	2.60			
XI	Propyl	C ₂₈ H ₅₈ BrNO ₂	520.67	64.59	11.23	2.69	81	—	0.52
				64.77	10.99	2.46			
XII	Isopropyl	C ₂₈ H ₅₈ BrNO ₂	520.67	64.59	11.23	2.69	89	—	0.55
				64.89	11.26	2.58			
XIII	Butyl	C ₂₉ H ₆₀ BrNO ₂	534.69	65.14	11.31	2.62	88	—	0.51
				64.75	11.42	2.52			
XIV	Pentyl	C ₃₀ H ₆₂ BrNO ₂	548.72	65.66	11.39	2.55	82	—	0.51
				65.42	11.60	2.30			
XV	Isopentyl	C ₃₀ H ₆₂ BrNO ₂	548.72	65.66	11.39	2.55	87	—	0.56
				65.42	11.15	2.58			
XVI	Hexyl	C ₃₁ H ₆₄ BrNO ₂	562.75	66.16	11.46	2.49	83	53—55 Capillary tube	0.50
				65.81	11.42	2.36			
XVII	Benzyl	C ₃₂ H ₅₈ BrNO ₂	568.71	67.60	10.28	2.46	80	44—46 Capillary tube	0.55
				67.40	9.99	2.25			

(X—XV) were oily compounds. Similar properties can be found in the literature [12] for the ammonium salts of esters derived from different carboxylic acids. Purification of these salts by extraction was found to be more advantageous than by column chromatography. Because it is unusual for the monoammonium salts with the relative molecular weights higher than 400 to be extremely hygroscopic, as it is in this case, we prepared didodecyldimethylammonium bromide (DMABr) which did not contain ester group. This compound was not hygroscopic and had a relatively high melting point. Also the compounds I—VIII, which did not contain esterified carboxyl groups, were not hygroscopic and had higher, sharp melting points. On the basis of this and of common knowledge of compounds of similar type it is possible to state that the present alkoxy-carbonyl group is responsible for the anomalous properties of the above-mentioned compounds.

In the i.r. spectra of esters we focused our attention first of all on the presence of the $\nu(\text{C}-\text{O}-\text{C})$ bands at $\sim 1200\text{ cm}^{-1}$ and $\nu(\text{C}=\text{O})$ at $\sim 1740\text{ cm}^{-1}$. We found that the band $\nu(\text{C}-\text{O}-\text{C})$ was with the ammonium salts the same as with the starting esters similarly as the $\nu(\text{C}=\text{O})$ bands which appeared in a narrow interval of $1742\text{--}1737\text{ cm}^{-1}$. Also the alkoxy group with either linear or branched chains had no observable influence on the frequencies of the $\nu(\text{C}=\text{O})$ bands (Table 3). We observed a broad band belonging to $\nu(\text{O}-\text{H})$ with all esters at $\sim 3415\text{ cm}^{-1}$, which indicated the presence of traces of moisture as a consequence of high hygroscopicity of the products. When comparing this phenomenon with DMABr which has no alkoxy-carbonyl group in its molecule and did not show the $\nu(\text{O}-\text{H})$ bands in the spectra, it is presumable that, in the case of esters, water is preferentially bound by the alkoxy-carbonyl group.

The i.r. spectra of ammonium salts having a free carboxyl group in their molecule were a specific problem. With regard to the presence of this group it is presumable

Table 3

Infrared spectral data (cm^{-1}) of dodecyl(10-alkoxy-carbonyldecyl)dimethylammonium bromides^a

Compound	$\nu(\text{C}-\text{O}-\text{C})$	$\nu(\text{C}=\text{O})$
<i>IX</i>	1177	1736
<i>X</i>	1183	1736
<i>XI</i>	1179	1735
<i>XII</i>	1181	1732
<i>XIII</i>	1177	1735
<i>XIV</i>	1174	1734
<i>XV</i>	1175	1734
<i>XVI</i>	1184	1731
<i>XVII</i>	1171	1735

a) Zeiss UR-10 in nujol.

that such compounds will be able to form dimers. The $\nu(\text{C}=\text{O})$ bands of dimers are dependent on the state and in solutions were observed in the region of 1720—1705 cm^{-1} . In crystalline state they appeared at about 1700 cm^{-1} . In the case of monomeric acids the $\nu(\text{C}=\text{O})$ band was observed in solutions at 1774—1735 cm^{-1} [13]. Similarly, the $\nu(\text{C}-\text{O})$ bands of the dimer appeared in the region of 1315—1280 cm^{-1} and those of the monomer in the region of 1190—1075 cm^{-1} [14].

When studying the i.r. spectra of ammonium salts of 11-aminoundecanoic acid in crystalline state we found that they differ essentially from those of the starting 11-bromoundecanoic acid which appeared in both KBr pellets and paraffin oil suspension as dimer. The dimer form predominated also in the solution (Table 4). The main difference between the spectra of the compounds investigated and those of the model was the absence of the characteristic broad absorption $\gamma(\text{O}-\text{H})$ band at $\sim 940 \text{ cm}^{-1}$.

Table 4

Stretching vibrations of carboxyl group (cm^{-1}) of alkyl(10-carboxydecyl)dimethylammonium bromides in crystalline state (A) and in CH_2Cl_2 solution (B)^a

Compound	$\nu(\text{C}=\text{O})$		$\nu(\text{C}-\text{O})$
	A	B	
I	1730	1724	1175
II	1727	1724	1176
III	1727	1724	1162 d
			1176
IV	1718 d	1724	1179
	1732		
V	1727	1724	1175
VI	1724	1724	1175
VII	1724	1724	1174
VIII	1728	1726	1174
BU ^b	1713	1711	1283
		1745 sh	

a) Perkin—Elmer 337, $c = 1 \times 10^{-2} \text{ M}$; b) 11-bromoundecanoic acid; $\delta(\text{O}-\text{H}) 940 \text{ cm}^{-1}$.
d — doublet, sh — shoulder.

The $\nu(\text{C}=\text{O})$ bands appeared in the solid state as an asymmetric absorption band in the region of 1732—1724 cm^{-1} . In one case (compound IV) this band was clearly split into doublet of the same intensity (Table 4). Such splittings of bands were not observed in solutions. With chosen compounds we found, in addition to the main band in the concentration range of 1×10^{-2} — $5 \times 10^{-3} \text{ M}$ in dichloromethane, two inflection points (Table 5). At higher concentrations only one

Table 5

Dependence of wavenumbers $\nu(\text{C}=\text{O})$ on concentration of alkyl(10-carboxydecyl)dimethylammonium bromides in CH_2Cl_2 solutions ($\bar{\nu}$, $\Delta\nu_{1/2}^a$ in cm^{-1} , ϵ^a in $\text{M}^{-1} \text{cm}^{-1}$)^a

Compound		1	2	3	4	$\Delta\nu_{1/2}^a$	ϵ^a
II	m	1725	1724	1726	1726	41	234
	i_1	1715	1713	1713	1715		
	i_2	—	—	1745	1740		
V	m	1724	1723	1726	1725	41	128
	i_1	1715	1713	1713	1714		
	i_2	—	—	1745	1742		
VIII	m	1724	1723	1726	1725	45	193
	i_1	1714	1713	1713	1713		
	i_2	—	—	1743	1740		

a) Zeiss UR-20.

1. $c = 1 \times 10^{-1}$ M, cells NaCl, $d = 0.25$ mm; 2. $c = 5 \times 10^{-2}$ M, cells NaCl, $d = 0.62$ mm; 3. $c = 1 \times 10^{-2}$ M, cells NaCl, $d = 2.27$ mm; 4. $c = 5 \times 10^{-3}$ M, cells NaCl, $d = 2.70$ mm.m — main band; i_1, i_2 — inflection points on the shoulders of the main band.

inflection point appeared in both dichloromethane and in the more polar methanol (Table 6). As can be seen from Table 5 the change of concentration has practically no effect on the shift of the wavenumbers of the main band. This indicates that the studied acids do not appear in dimer form.

The half-width of the band ($\Delta\nu_{1/2}^a$) differed only slightly when the spectra were taken in weak polar and polar solvents. However, the difference in the intensity, expressed as molar absorption coefficient (ϵ^a), was evident. The ϵ^a values obtained in polar solvents were lower. They were not proportional to molecular weight in either solvent probably due to the presence of satellite bands which appeared on the shoulder of the main band as inflection points (Tables 5 and 6).

Table 6

Stretching vibrations of alkyl(10-carboxydecyl)dimethylammonium bromides in methanol ($\bar{\nu}$, $\Delta\nu_{1/2}^a$ in cm^{-1} , ϵ^a in $\text{M}^{-1} \text{cm}^{-1}$)^a

Compound	$\nu(\text{C}=\text{O})^b$	$\Delta\nu_{1/2}^a$	ϵ^a	i
II	1732	42	168	1719
V	1729	43	121	1717
VIII	1729	42	137	1716

a) Zeiss UR-20, $c = 8 \times 10^{-2}$ M, cells CaF_2 , $d = 0.40$ mm.

b) Main band.

 i — inflection point.

The further important band of these compounds was the $\nu(\text{C}-\text{O})$ band (Table 4). On the basis of the position of this band it is possible to assume that the compounds studied do not appear in the dimer form. It is evident also from the absence of the $\delta(\text{O}-\text{H})$ band in the spectra of these compounds, which is characteristic of dimeric acids (the region of $960-875\text{ cm}^{-1}$) [15].

With the compounds investigated the $\nu(\text{C}=\text{O})$ band in solution (Table 4) was observed in the region where bands characteristic of monomeric and dimeric forms of carboxylic acids appeared (constantly at 1724 cm^{-1}) except the compound VIII (1726 cm^{-1}). On the basis of this knowledge and comparison with the literature data [16, 17] (the paper [16] gives the characteristic absorption band $\nu(\text{C}=\text{O})$ for cetyldimethylammoniumacetobetaine chloride at 1725 cm^{-1}) it is possible to assume that the studied compounds have the following structure



This structure explains the absence of the $\nu(\text{O}-\text{H})$ and $\delta(\text{O}-\text{H})$ bands in the spectra of the compounds investigated (in contrast to the spectrum of 11-bromo-undecanoic acid).

In the $^1\text{H-n.m.r.}$ spectra of the ammonium salts bands belonging to the signals of protons of OH were not found in contrast with 11-bromoundecanoic acid, where a significant signal $\delta = 9.67\text{ p.p.m.}$ was observed similarly as with alkanecarboxylic acids [18].

Also the determination of molecular weights with some chosen compounds showed that they did not appear in dimer form (Table 1).

On the basis of the determined $\text{p}K_{\text{A}}$ values of these compounds (Table 1) it can be stated that they have the betaine structure because the $\text{p}K_{\text{A}}$ values of the alkanecarboxylic acids are about 5 [19].

As a complementary method to i.r. spectroscopy we used Raman spectroscopy. In the Raman spectra the absorption band $\nu_s(\text{C}=\text{O})$ should appear with dimeric acids in the region of $1680-1640\text{ cm}^{-1}$ [14]. We have not observed in this region ($1700-1600\text{ cm}^{-1}$) any absorption band, therefore, it can be assumed that the compounds investigated do not appear in dimeric form.

Acknowledgements. We thank Ing. M. Pisárčik, CSc. (Slovak Academy of Sciences, Bratislava), Dr. J. Vanžura (Faculty of Pharmacy, Charles University, Hradec Králové), Dr. E. Dvořáková, K. Révayová, and Dr. V. Hartelová (Faculty of Pharmacy, Komenský University, Bratislava) for cooperation.

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Translated by A. Kardošová