SYNTHESIS AND SPECTRAL PROPERTIES OF SHIELDED 1,2-DISUBSTITUTED IMIDAZOLINES

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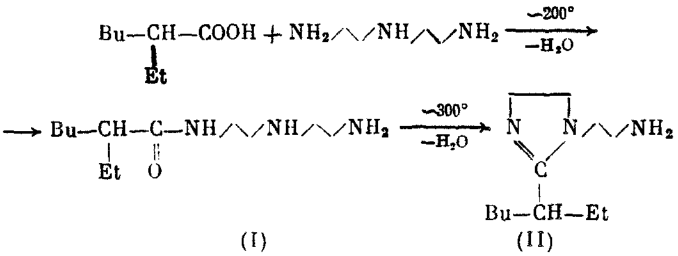
Shielded 1,2-disubstituted imidazolines were synthesized by condensation of diethylenetriamine with 2-ethylhexanoic acid. UV, IR and ^{1}H and ^{13}C NMR spectral data were discussed. The effect was studied of α branching in an alkyl substituent at the 2 position of the imidazoline ring on the spectral parameters of the synthesized compounds.

There are a large number of works devoted to the syntesis and study of 1,2-disubstituted imidazolines because of their wide use as raw material for production of cationic and amphoteric surface active substances [1]. However, there is very little data in the literature on 1,2-disubstituted imidazolines with an α-branched alkyl substituent on the second carbon atom of the ring although it would be expected that the stability to the action of aggressive media and elevated temperatures [2] of the compounds, resulting from the shielding effect of the substituent, would increase. In this work the effect was studied of an α-branched alkyl substituent on the spectral properties of several condensation products of diethylenetriamine (DETA) with 2-ethylhexanoic acid (EHA).

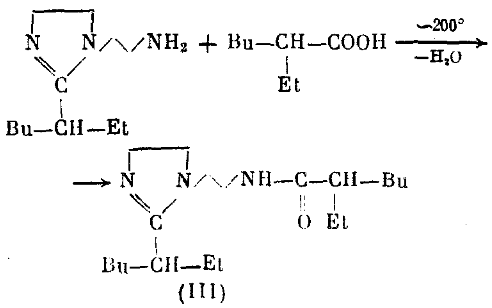
RESULTS AND DISCUSSION

The products were synthesized according to the following scheme:



(I) (II)

Compound (III) is obtained preferentially in an excess of EHA:



(III)

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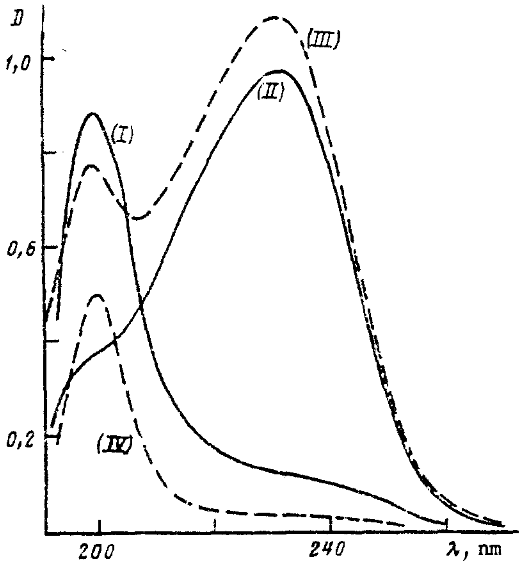

Fig. 1. UV spectra of solutions of compounds (I) ($c = 1.25 \cdot 10^{-3}$ mole/liter), (II), (III) ($c = 0.75 \cdot 10^{-3}$ mole/liter) and DETA (IV) ($c = 5.00 \cdot 10^{-2}$ mole/liter) in ethanol, $\ell = 2$ mm, T = 23°C.

It is known that condensation of straight chain carboxylic acids with DETA with the formation of amides and subsequent cyclization of the amides to imidazolines goes with marked speed at 160-180 and 200-250°C, respectively [1, 3]. However, in the case of condensation of 2-ethylhexanoic acid with DETA, elevated temperatures are required for obtaining the corresponding products which is evidently due to a steric factor [2]. In addition, a definite influence is probably caused by the positive induction effect (+I effect) of the α-branched alkyl substituent which hinders ionization of the carboxylic acid.

In the 200-240 nm region of the UV spectra of all the compounds there are two absorption bands (Fig. 1). In going to a less polar solvent (water—ethanol—hexane) the shortwave bands of all compounds undergo a bathochromic shift ($\Delta\lambda = 8$-9 nm) and the longwave bands of compounds (II) and (III) are shifted toward the short-wavelength side ($\Delta\lambda = 3$-4 nm). When the solutions are acidified the short wave band in the spectrum of (II) disappears and the intensity of the corresponding bands for (I) and (III) are noticeably decreased. Thus, it can be postulated that the shortwave bands in the spectra of (I) and (III) are due to both the presence of the $\mathrm{NH{-}\underset{|}{C}{=}O}$ group and $n \rightarrow \sigma^*$ transitions in NH and NH_2 groups, and in the spectrum of (II) only due to an $n \rightarrow \sigma^*$ transition in an NH_2 group. The intense longwave bands in the spectra of (II) and (III) correspond to a $\pi \rightarrow \pi^*$ transition of the C=N bond in the hetero ring [3, 4]. Comparison of the UV spectra with those of [3-5] showed that the +I effect caused by the branched alkyl substituent leads to a weak bathochromic shift in the maximum of the $\pi \rightarrow \pi^*$ band. Here the values of the molecular absorption coefficients hardly change.

The IR spectra of compounds (I)-(III) and of similar compounds having linear alkyl substituents are analogous; however, small shifts ($\Delta\nu = 10$-15 cm^{-1}) are noted for the most characteristic absorption frequencies, which evidently should be related to the +I effect also.

^{1}H and ^{13}C NMR spectroscopy of similar compounds has not been studied sufficiently [5-8]. Therefore, we carried out a detailed study of the synthesized compounds using these methods. In the PMR spectra of (I) and (III) the proton of the amide group is manifested in the form of a broadened signal in the 6.4-6.5 ppm region. In the case of (II) this signal is absent and multiplet signals from the strongly bonded four-spin system AA'BB' of the methylene protons of the imidazoline ring are observed in the regions 3.10-3.37 and 3.57-82 ppm (operating frequency 100 MHz) (Table 1). At an operating frequency of 300 MHz the proton spin system of the ring is transformed into A_2X_2 with coupling constant $J_{AB} = 9.7$ Hz.

In the ^{13}C NMR spectra the strong field signals correspond to the branched hydrocarbon radical (Table 2). Triplet signals at 38-51 ppm characterize methylene carbon atoms bound to a nitrogen atom. The differences in the spectra of (I) and (II) are probably explained by formation of the imidazoline ring. Weak field signals of sp^2 hybridization are most characteristic for this. In the spectrum of compound (I) this weak field singlet is at

TABLE 1. PMR Spectra of Compounds (I)-(III) (δ, ppm, $CDCl_3$, TMS, 100 MHz)

Fragment	Proton chemical shifts and coupling constants		
	(I)	(II) *	(III)
CH_3	0,88 t; 7,0 Hz	0,88 t; 7,0 Hz	0,88 t; 7,0 Hz
CH_2	1,28 m (4H)	1,28 m (4H)	1,28 m (4H)
$\underline{CH_2}-CH$	1,43 m (4H)	1,57 m (4H)	1,55 m (8H)
$\underline{CH}-C(=O)-NH$	1,92 m	–	1,92 m
$CH-C(-)=$	–	2,26 m	2,16 m
$\underline{CH_2}-NH$, $\underline{CH_2}-NH_2$	2,76 m (6H)	2,85 t (2H); 6,2 Hz	–
$CH_2-N(-)-$	3,34 m (2H)	3,16 t (2H); 6,2 Hz 3,27 t (2H); 9,7 Hz	3,10–3,36 m (6H)
$CH_2-N=C$	–	3,68 t (2H); 9,7 Hz	3,61–3,79 m (2H)
NH, NH_2	1,28 br.s (1H) 1,43 s (2H)	1,80 br.s (2H)	–
$NH-C(-)=O$	6,38 br.s	–	6,53 br.s

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*Data obtained at an operating frequency of 300 MHz.

TABLE 2. ^{13}C NMR Spectra of Compounds (I)-(III) (δ, ppm, $CDCl_3$, TMS)

Fragment	Carbon chemical shifts		
	(I)	(II)	(III)
CH_3	11,88 q; 13,77 q	11,94 q; 14,10 q	11,88 q; 12,14 q 13,97 q
CH_2	22,52 t; 25,85 t; 29,64 t; 32,31 t	22,91 t; 26,63 t; 29,76 t; 33,16 t	22,78 t; 22,91 t 25,98 t; 26,50 t 26,69 t; 29,76 t 32,44 t; 33,09 t
$\underline{CH}-C(-)=$	–	38,51 d	38,58 d
$\underline{CH}-C(=O)-NH$	49,23 d	–	49,67 d
$CH_2-N(-)-$	38,71 t; 41,32 t	40,93 t; 50,33 t	38,06 t; 46,93 t
$-C(-)=N$	48,57 t; 51,50 t –	50,72 t; 52,09 t 170,70 s	50,63 t; 52,16 t 170,43 s
$-C(=O)-NH$	176,05 s	–	176,11 s

176.05 ppm, which represents an amide group [9] and in the spectrum of (II) the singlet at 170.70 ppm corresponds to a double-bonded carbon atom with an sp^2 hybridized nitrogen atom [10]. Both signals are present in the spectrum of (III). The observed paramagnetic shifts of the signals of the sp^2 hybridized atoms ($\Delta\delta$ = 2-3 ppm) in comparison with the analogous compounds with linear alkyl substituents [5] should also be explained by the β effect of the ethyl substitutent [11].

Thus, the presence of an ethyl group in the α position of the alkyl substituent leads in this case to a shift of the spectral properties of the synthesized compounds without changing their character.

EXPERIMENTAL

The compounds were prepared by condensation of anhydrous DETA with EHA at a mole ratio of 1.0:0.7-2.0 in a stream of nitrogen at 200-300°C. Purity was controlled by gas-liquid chromatography [12] with a Khrom-5 chromatograph in a stream of He, column 1.2 m × 3 mm with 15% SE-30 on Khromaton N-AW. UV spectra were taken on a Specord UV-VIS and Specord UV-VIS M 40 at 51-28,000 cm^{-1}. IR spectra were obtained on a UR-20 spectrophotometer using a film. ^{13}C NMR spectra were taken on a Jeol FX-90Q pulse spectrometer with an operating frequency of 22.5 MHz with wide band proton quenching in "monoresonance" conditions. PMR spectra were obtained with a Tesla BS-567 Fourier transform pulse spectrometer (100 MHz) and with a Bruker AM-300 (300 MHz) spectrometer. The solvent was $CDCl_3$ and internal standard TMS. Molecular masses of the synthesized compounds were determined by measuring the thermal effects of condensation in a standard and in ethyl acetate by the method of [13].

N-(3-Aza-5-aminopentyl)-2-ethylhexanamide (I). To 14.4 g EHA is added with stirring 15.5 g DETA and the solution held for 1 h at 90 ± 5°C, then for 3 h at 210 ± 5°C and cooled to ~20°C, followed by vacuum distillation at 160-162°C (5 mm) to yield 11.0 g (48%) (I). UV spectrum, λ_{max}, nm (ε, liter/(mole·cm): 203 (3540), 236 (500). IR spectrum, ν, cm^{-1}: (1650, 1560 (NH—C=O)).

1-(2-Aminoethyl)-2-(1-ethylpentyl)-4,5-dihydroimidazole (II). To 14.4 g EHA is added with stirring 15.5 g DETA, the solution held for 1 h at 90 ± 5°C, 3 h at 210° ± 5°C, 5 h at 300 ± 5°C, and cooled in a stream of nitrogen to ~20°C. Vacuum distillation yielded 11.6 g (55%) (II), bp 138-140°C (10 mm). UV spectrum, λ_{max}, nm (ε, liter/(mole·cm)): 203 (2500), 232 (6200). IR spectrum (ν, cm^{-1}): 1610 (C=N), 1015 (C—N).

1-(5-Ethyl-4-oxo-3-azanonyl)-2-(1-ethylpentyl)-4,5-dihydroimidazole (III). To 28.8 g EHA is added 10.3 g DETA with stirring and the solution held 1 h at 90 ± 5°C, 4.5 h at 200 ± 5°C, and cooled to ~20°C. Vacuum distillation yielded 15 g (44%) (III), bp 205-207°C (5 mm). UV spectrum, λ_{max}, nm (ε, liter/(mole·cm)): 203 (5000), 233 (7200). IR spectrum (ν, cm^{-1}): 1650, 1565 (—NH—C=O), 1610 (C=N), 1015 (C—N).

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