SPECTRAL AND POLAROGRAPHIC CHARACTERISTICS OF CERTAIN N-(2-HYDROXYETHYL) ALKYLIDENAMINES

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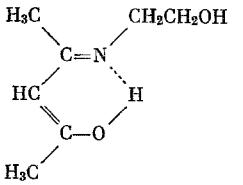
Azomethine compounds are characterized by rapid conformational and configurational transitions [1, 2]. The ease of transfer of charge in the C=N group determines a number of specific properties of azomethines, for example, the ability for oxidation [2] and the formation of complexes with metals [3, 4]. As a result of this, they are finding use in catalysis [5, 6], in biochemical investigations [7], and in the synthesis of heat-stable polymers of the chelate type [8]. Examples are known of the practical application of azomethines as stabilizers of oils [9] and extraction reagents for rare metals [10].

In this work we obtained some spectral (IR, PMR) and polarographic characteristics of N-(2-hydroxyethyl) alkylidenamines. The N-(2-hydroxyethyl) alkylidenamines (HEA) were produced by the reaction of condensation of ethanolamine with ketones.

IR Spectra. The values of the absorption frequencies of the basic groups of HEA and certain cyclic azomethines are cited in Table 1. As it follows from Table 1, the valence vibration of the C=N group in HEA, with the exception of compound (VII), varies little with the nature of the substitution, both on the part of the carbon atom and on the part of the nitrogen atom. In HEA there is an intramolecular H-bond. According to the data of the spectra for the compounds (III), (IV), and (VII) in CCl_4 solution ($C = 2 \cdot 10^{-3}$ M), the H-bond leads to only a small increase in the frequency $\nu_{N=C}$ (by 3-6 cm^{-1}) when the valence vibration of the OH group is changed by 100-200 cm^{-1}.

The bands of the valence vibration of the azomethine group in compounds (I)-(VI), (VIII), and (IX) lie in the interval 1600-1668 cm^{-1}, for the compound (VII) $\nu_{C=N}$ is in the region of 1605 cm^{-1} and $\nu_{C=CH}$ in the region of 1550 cm^{-1} (in CCl_4 and THF solution 1615 and 1584 cm^{-1}, respectively). The low frequency shift of the band of the valence vibration by 50 cm^{-1} in comparison with the usual value for $\nu_{C=N}$ [12, 13] is evidently due to keto – enol tautomerism. It will be shown below that the azomethine (VII) exists in an enol form, which is stabilized by the formation of a conjugated six-membered ring on account of a hydrogen bond:



The value of $\nu_{C=N}$ in the series of cyclic azomethines (X)-(XIII) also varies little with the nature of the substitution. As can be seen from Table 1, the frequency of the valence vibrations of the C=N bonds, involved in the chain of conjugation [compound (X)-(XI)] and standing next to the electron-donor group HN [compound (XII)] differs by 2-5 cm^{-1}, but the electron-donor group $\diagdown\overset{+}{\mathrm{N}}\diagup$ in (XIII) shifts the valence vibration by 5 cm^{-1} into the high-frequency region of the spectrum and increases the absorption intensity.

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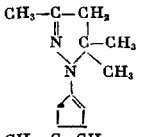
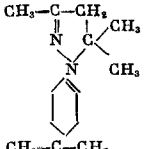
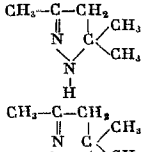
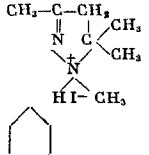
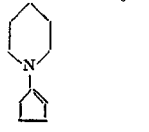
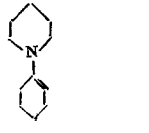
TABLE 1. Absorption Frequencies (in cm^{-1}) of the Basic Groups of N-(2-Hydroxyethyl) Alkylidenamines and Certain Cyclic Azomethines

Compound	Formula	$\nu_{C=N}$	ν_{OH}	$\delta_{CH_3C=N}$	Compound	Formula	$\nu_{C=N}$	$\delta_{CH_3C=N}$	$\nu_{HC=CH}$
(I)	$(CH_3)_2C{=}NCH_2CH_2OH$	1667 v. s.	3200 3430	1373					
(II)	$CH_3CH_2C(CH_3){=}NCH_2CH_2OH$	1660 v. s	3310	1376	(X)		1620 s	1330 1360	1632 v. s 3080
(III)	$(CH_3)_2CHCH_2C(CH_3){=}NCH_2CH_2OH$	1666 v. s	3200 3440	1373	(XI)		1623 s	1340 1360	1643 v. s 3070
(IV)	$CH_3C(CH_2CH{=}CH_2){=}NCH_2CH_2OH$	1664 v. s 1646 ($\nu_{CH_2=CH}$)	3320	1390	(XII)		1625 w	1320 1380	
(V)	$C_6H_{10}C{=}NCH_2CH_2OH$	1667 v. s	3310						
(VI)	$C_6H_5C(CH_3){=}NCH_2CH_2OH$	1667 v. s	3200 3450	1372	(XIII)		1630	1345 1390	
(VII)	$CH_3C(CH{=}COH(CH_3)){=}NCH_2CH_2OH$	1605 v. s 1550 v. s ($\nu_{C=CH}$)	3300	1343 1371					
(VIII)	$CH_3CH_2C(CH_3){=}NCH_2CH_2CH_2CH_3$	1668 v. s		1385	(XIV)				1630 v. s 3065 [11]
(IX)	$(CH_3)_2C{=}NN{=}C(CH_3)_2$	1660 v. s		1375	(XV)				1642 v. s 3063 [11]

The IR spectra were taken in KBr.

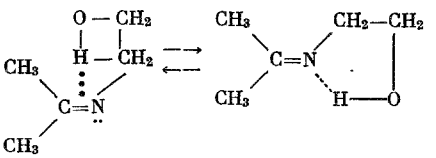
TABLE 2. Chemical Shifts (δ, ppm) of the Protons of N-(2-Hydroxyethyl) Alkylidenamines

Compound	In CCl_4 solution				In C_6H_6 solution				Ratio of anti- and syn-isomers
	$CH_3C=N$	$=NCH_2$	$-CH_2O-$	R	$CH_3C=N$	$=NCH_2$	$-CH_2O-$	R	
(I)	1,25	3,21	3,62	1,25	1,39 1,16	2,75 3,16	3,45 3,82	1,39 1,16	2,3 : 1
(II)	1,14	2,95	3,56	0,76; 1,30	1,35 1,10	2,65 3,10	3,36 3,75	0,82; 1,45	5 : 1
(III)	1,20	2,85 3,21	3,25 3,60	0,93; 1,45	1,35 1,16	2,69 3,11	3,39 3,80	0,86; 1,75	1,2 : 1
(IV)	1,30 1,23	2,64 3,01	3,26 3,60	4,95 5,69 $CH_2=CH$	1,26 1,10	2,61 3,05	3,43 3,69	4,90 5,55 $CH_2=CH$	3,5 : 0,8
(V)	—	3,02	3,60	1,48	—	2,65	3,37	1,45	1 : 0
(VI)	2,20 1,55	3,50	3,75	7,27 7,50	1,67 1,47	2,55 3,22	3,39 3,85		1,5 : 1
(VII)	1,85	3,36	3,64	1,91; 4,81	1,45	2,90	3,45	1,90; 4,75 4,94	1 : 0

From the IR spectra of compounds (I)-(XIII) it follows that the frequency of the C=N valence vibration is relatively insensitive to electron-donor substituents, to conjugation both on the part of the carbon atom and on the part of the nitrogen atom, as well as to the participation of the azomethine group in the formation of an intramolecular H-bond.

PMR Spectra. The values of the chemical shifts for solutions of HEA in CCl_4 and benzene are cited in Table 2. In the compounds (II)-(IV) and (VI), two groups of signals from the protons of NCH_2CH_2O and alkyl radicals are observed, which is evidence of the existence of azomethines in two configurations (syn- and anti-isomers) [14, 15]. In the transition from CCl_4 to benzene, as a result of the stereospecific $p-\pi$-interaction of the azomethine molecules with the aromatic solvent, the signals of the protons of the anti-isomer are shifted into a strong field, while those of the syn-isomer are shifted into a weak field [15]. On the basis of the fact that hydrazones isomerize into a thermodynamically unstable syn-form in acid media [15], we can assume that the intramolecular H-bond should stabilize the syn-isomer to a greater degree and shift the equilibrium in the direction of the syn-form. According to the data of the PMR spectra (see Table 2), azomethines with alkyl substituents are more readily converted to the syn-form. The compound (VII) exists in one isomeric form. According to the change in the chemical shifts of the protons of the molecule in benzene [15], it has an exclusively anti-configuration.

Although the structure of compounds (I)-(V) excludes configurational isomerism, however, in the PMR spectrum of the azomethine (I) for benzene solution two groups of signals from the protons of $NCH_2 \cdot CH_2OH$ and CH_3 appear (Fig. 1), while in the spectrum of the azomethine (V) the signals of the protons of NCH_2CH_2OH are shifted in the strong-field direction. Two symmetrical triplets (Fig. 1a), 3.21 and 3.62 ppm, belong to the NCH_2CH_2O group; the broad signal in the region of 1.9 ppm belongs to the proton of the bound hydroxyl, while the singlet 1.25 ppm belongs to the protons of the methyl groups. In benzene solution (Fig. 1b), each signal is separated into two. The signals in a low field 3.16 and 3.82 ppm (NCH_2CH_2O), 2.11 (OH), and 1.39 ppm (CH_3) evidently belong to one isomer; the signals 2.75 and 3.45 ppm (NCH_2CH_2O), 1.9 ppm (OH), and 1.16 ppm (CH_3) belong to the other isomer. The ratio of the isomers is ~1 : 2.3. The separation of the signals from the protons of compound (I) into two groups in benzene solution may be caused by rotational isomerism and the existence of the azomethine (I) in two stable configuration at room temperature:



The azomethine (VII) exists in an enol form: the signal from the methine proton of the HOC=CH group for a solution in CCl_4 has a chemical shift of 4.81 ppm; the signal of the hydroxyl proton in $CDCl_3$ solution appears as a broad singlet (4.94 ppm); upon dilution it is shifted in the strong-field direction on account of the formation of a H-bond. In the spectra of (VI) and (VII), the signal from the hydroxyl proton

TABLE 3. Polarographic Characteristics of N-(2-Hydroxyethyl) Alkylidenamines

Compound	$-E_{1/2}$, V	pH of supporting electrolyte	Compound	$-E_{1/2}$, V	pH of supporting electrolyte
(I)	1,87	10,5	(VIII)	1,77	10,5
(II)	1,85	10,5	(IX)	1,68	7,7
(III)	1,89	10,5	(X)	1,66	9,0
(IV)	1,83	10,5	(XI)	1,65	9,0
(V)	1,80	11,1	(XII)	1,37	9,0
(VI)	1,54	10,5			

for solutions of CCl_4 does not appear. The signal from the bound hydroxyl proton for solutions of the azomethines (I)-(V) in CCl_4 lies in the region of 2.0-2.2 ppm; in $CDCl_3$ the signal from the OH proton in the spectrum of compound (V) appears at 1.93 ppm; when the concentration is increased, the signal is shifted in the weak-field direction.

Polarographic Reduction. The relationship between the structure of the compounds with an azomethine group in the molecule and their polarographic properties has been investigated chiefly for the examples of reduction of aromatic azomethine bases [16, 17]. The following reduction scheme is assumed for them

$$\begin{matrix} PhC{=}NPh \\ | \\ R \end{matrix} + 2e + 2H^+ \rightleftarrows \begin{matrix} PhCHNHPh \\ | \\ R \end{matrix}$$

We conducted a polarographic reduction of HEA in 50% CH_3CN* with a buffer solution (0.05 M $Na_2B_4O_7 \cdot 10H_2O$ – NaOH; pH 9.18) as the supporting electrolyte. For comparison, the reduction of the compounds (IX)-(XII), the C=N group of which is included in a chain of conjugation, was conducted under the same conditions. As can be seen from Table 3, in the interval of pH 7-12 all the azomethine bases form one wave. The value of the half-wave potentials ($-E_{1/2}$) depends on the structural properties of the azomethines. The increase in electron density of the $\diagdown C{=}N\diagup$ bond in the azomethines (I)-(V) produces a shift of the reduction potentials in the direction of more negative values.

It is known that at pH 10-11 certain aromatic azomethines with a system of conjugation are reduced through the stage of electron transfer and in almost the same region of potentials ($-E_{1/2}$ = 1.65-1.80 V [16]). This leads to the idea that in the region of pH 7-12 the reduction of HEA evidently proceeds through the stage of transfer of an electron to a nonprotonated molecule, but requires more negative potentials.

The alkylidenamine (II) is reduced with substantially greater difficulty than isopropylidenebutylamine (VIII) [$\Delta E_{1/2}$ for (II) and (VIII) is 80 mV]. According to the induction constants, for the 2-hydroxyethyl and butyl groups we should have expected the reverse effect in electroreduction. The cause of the more difficult reduction of the azomethine (II) on the cathode, which plays the role of a nucleophilic reagent under these conditions, is an increase in the electron density of the $\diagdown C{=}N\diagup$ group on account of the formation of an intramolecular H-bond [16].

The introduction of the azomethine bond into the chain of conjugation [compounds (IX)-(XI)] and the lengthening of the chain of conjugation [compound (VI)] increase the polarographic activity of the compounds by 150-300 mV. The azomethine (VII) and the vinylamines (XIV) and (XV) (see Table 1) are not polarographically active under these conditions.

It should be noted that the value of the half-wave potential expresses the summary electronic effect of the molecule, and therefore, in the case of reduction on the cathode, no configurational differences of the HEA are manifested.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 spectrophotometer in a thin layer and in a solution of CCl_4 at a concentration of $(2\text{-}5) \cdot 10^{-3}$ M.

*In DMFA and methanol solution, a pronounced wave of azomethine could not be obtained.

TABLE 4. Physicochemical Characteristics of N-(2-Hydroxyethyl) Alkylidenamines

Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	N, % found	N, % calculated
(I)	83,0	36—37(17)	1,4500	0,9600	29,10	28,90	13,72	13,80
(II)	93,0	54—56(22)	1,4415	0,9308	33,75	33,53	12,02	12,20
(III)	95,0	90—93(16)	1,4585	0,9008	43,03	43,85	10,30	9,80
(IV)	94,7	99(26)	1,4640	0,9216	39,99	39,24	9,95	9,90
(V)	73,0	88—89(15)	1,4835	1,0124	40,97	40,70	10,10	9,91
(VI)	98,7	143—144(16)	1,5542	1,0691	48,85	48,86	8,54	8,60
(VII)	72,2	Bp. 69—70	—	—	—	—	10,38	9,79

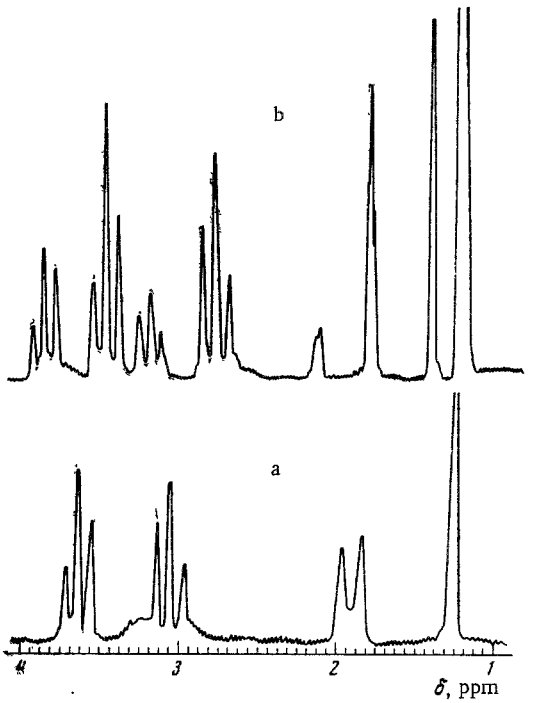


Fig. 1. PMR spectrum of N-(2-hydroxyethyl) isopropylidenamine (I): a) in CCl_4; b) in C_6H_6.

The PMR spectra were recorded for 5-10% solutions in CCl_4 and C_6H_6 on a Tesla BS 487C instrument at 80 MHz relative to HMDS. The ratio of the anti- and syn-isomers was determined by a comparison of the integral intensities of the signals from the CH_3 and NCH_2CH_2O protons. The spin – spin interaction constant of the vicinal protons of NCH_2CH_2O is equal to 5-6 Hz.

The polarographic measurements of $E_{1/2}$ were conducted on an ON-101/1 polarograph. The characteristics of the electrode with forced breakoff of the drops were: m = 3.0 mg/sec, T = 2.8 sec [at E = 2.0 V in 50% CH_3CN against a background of 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ or 0.05 M $(C_2H_5)_4NI$]. The potential pertains to a saturated calomel electrode. Oxygen was removed from the cell and solution by purging with argon. The investigated solutions were prepared by diluting a 10^{-1} M solution of the azomethine in abs. CH_3CN with a solution of the supporting electrolyte. The concentration of the depolarizer was $(1-2) \cdot 10^{-3}$ M.

The alkylidenamines (I)-(VII) were produced for the first time, by condensation of ethanolamine with ketones. The reaction mixture, consisting of 2 moles of the ketone and 1.5 moles of monoethanolamine and 120 ml of benzene was heated to the boiling point of benzene with mixing. Water was distilled off in the form of an azeotrope with benzene into a water-clarifying tank. The end of the condensation reaction was judged according to the volume of the water liberated. The physicochemical characteristics are cited in Table 4. Compounds (IX)-(XV) (see Table 1) were produced according to the method of [11]. The purity of the azomethines was monitored by the method of gas – liquid chromatography (LKhM-7A chromatograph, column 300 × 0.4 cm, 15% apiezon L on chromaton, carrier gas helium, 210°).

CONCLUSIONS

1. A series of N-(2-hydroxyethyl) alkylidenamines (HEA) was produced by the condensation of ethanolamine with ketones.

2. The frequency of the C=N valence vibration in the IR spectra of HEA depends little on the electronic structure of C,N-substituents.

3. According to the data of the PMR spectra, HEA exists in two configurations (syn- and anti-isomers).

4. The polarographic reduction of HEA was studied; a dependence of the half-wave potential on the existence of an intramolecular hydrogen bond is observed.

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