IR SPECTRA AND STRUCTURE OF CERTAIN AMINO ACIDS IN SOLUTIONS AND IN THE GAS PHASE. DIBUTYLGLYCINE AND GLYCINE

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The simplest amino acids (AA) and their derivatives exist in the crystalline phase or in aqueous solutions in ionic form [1-6]. The results of calculations performed for the glycine molecule by an expanded Hückel method led the authors of [7] to conclude that the zwitterion form is also energetically stable in the case of the isolated molecule.

The as yet few experimental investigations of AA in relatively nonpolar surroundings (solutions in CCl_4, $CHCl_3$ [8, 9], matrices of Ar [10]) indicate a molecular structure of AA or the presence of equilibrium between the molecule and zwitterion forms. In view of this, it is of interest to investigate the influence of the properties of the medium on the structure of AA and on the possibility of the realization of intra- and intermolecular proton transfer. For this purpose, in the present work we recorded the IR spectra of vapors of glycine and N, N-dibutylglycine (DBG), as well as the spectra of solutions of DBG, which possesses satisfactory solubility in a number of solvents with various properties.

The IR spectra were recorded on a UR-20 spectrophotometer. In the recording of the spectra of the solutions, transmission of the solvents was no less than 25%. At temperatures exceeding the boiling point of the solvent, at normal pressure, the cuvette described in [11] was used. The spectra of the vapors were obtained with a quartz cuvette 75 mm long. Fluorite windows were clamped to the end of the cuvette through thermostable rubber gaskets. To remove traces of water, the cuvette with crystalline AA was conditioned under vacuum at temperatures of 100-150°C, then evacuated and sealed off from the vacuum apparatus. We synthesized DBG according to the method described in [9]. The purity of all the substances was monitored spectroscopically.

Figure 1a presents the spectra of solutions of DBG in CH_3OH and CCl_4. In the spectrum of a solution in methanol, a band with frequency 1640 cm^{-1} is observed, characteristic of the vibration $\nu_a CO_2^-$ of the ionized carboxyl group. The position and intensity of the band are unchanged with changing concentration or temperature of the solution, as well as with replacement of methanol by ethanol. An analogous band (1620 cm^{-1}) is also present in the spectrum of a solution of D_2O. Thus, in alcohol just as in aqueous solutions, DBG exists in a zwitterion form $HN^+R_2CH_2CO_2^-$ (M*).† In this case the CO_2^- and R_2NH^+ groups are evidently bonded by a hydrogen bond to the solvent molecules. In the spectrum of a solution in CCl_4, however, at a concentration ~ 10^{-4} M, determined by the solubility of DBG, the band 1770 cm^{-1} is observed, as well as a very weak band 3530 cm^{-1}, characteristic of the free hydroxyl group. It is natural to assume that the band 1770 cm^{-1} belongs to the vibration $\nu C=O$ of the DBG molecules present in solution in neutral form NR_2CH_2COOH (M). The presence of ionic forms could not be detected in solution in CCl_4.

Higher concentrations of DBG (up to 10^{-2} M) can be obtained in solutions with C_6H_6, C_6H_5Cl, and C_2HCl_3, the molecules of which possess proton acceptor capacity. In this case, in the region of 1600-1800 cm^{-1} at room temperature, two bands are observed– in the region of 1635-1640 and 1765 cm^{-1} (Fig. 1b, c). When the temperature is increased, as when the concentration decreases, the intensity of the band 1640 cm^{-1} falls, while that of the band 1765 cm^{-1} rises. At the temperature 120°C, only the band 1765 cm^{-1}, analogous to the band in the spectrum of a solution in CCl_4, remains in the spectrum of a solution in C_6H_5Cl. Undoubtedly this band belongs to DBG monomers of the M type. This is also confirmed by the appearance of the bands νOH with increas-

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†According to [5], the band around 1620 cm^{-1} is characteristic of the zwitterion form of glycine and other AA in aqueous solutions in a broad range of pH (pD); the band of the anion, lying 30-40 cm^{-1} lower, appears in D_2O at pD ~ 10-12.

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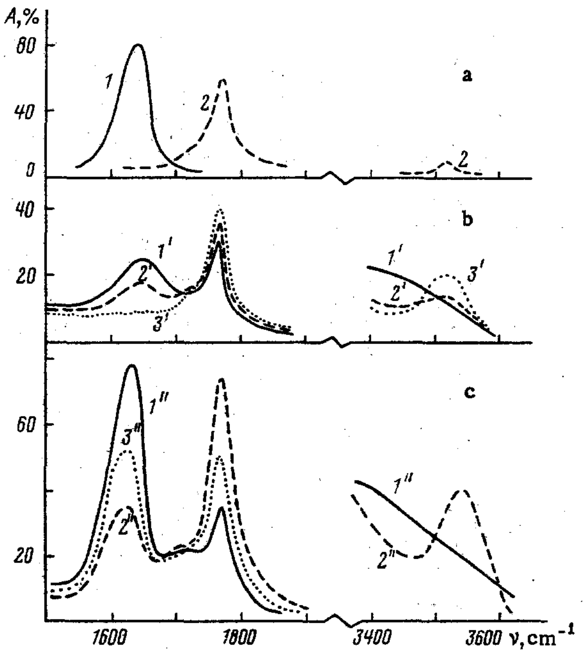
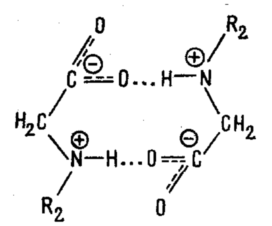


Fig. 1. Spectra of solutions of DBG in CH_3OH, 0.3 M (1); CCl_4, 0.00026 M (2); C_6H_5Cl, 0.025 M (1'-3'); C_2HCl_3, 0.05 M (1", 2") and 0.005 M (3"); T = 26 (1, 1', 2, 1", 3"), 50 (2'), 110 (3'), 80°C (2").

ing temperature (3510 cm^{-1} in C_6H_6 and C_6H_5Cl and 3520 cm^{-1} in C_2HCl_3). The behavior of the band 1640 cm^{-1} is the basis for taking it as dimeric. Since the value 1640 cm^{-1} is typical of $\nu_a CO_2^-$, it is evident that the dimer has an ionic structure of the type



(D*)

This conclusion agrees with the results of [8, 9]. Thus, in the enumerated solvents there is an equilibrium between the molecular monomers and ionic dimers

$$2M \rightleftharpoons D^*. \tag{1}$$

The picture is complicated for a strong polar solvent–acetonitrile (Fig. 2a). In the case of a solution of DBG in CH_3CN at concentrations $\sim 10^{-1}$ M, the band of the molecular form with frequency 1760 cm^{-1} has low intensity at room temperature. The band of the ionic form is an intense doublet with frequencies ~1635 and ~1650 cm^{-1}. When the concentration is lowered to $\sim 10^{-3}$ M, the intensity of the low-frequency component of the doublet is substantially reduced. An increase in the temperature at such concentrations leads to an increase in the intensity of the band of the molecular form at the expense of the band 1650 cm^{-1}. At the temperature 72°C the intensities of these two bands become of the same order of magnitude. These changes can be explained as follows. The band 1635 cm^{-1} belongs to dimers, while monomers exist in two forms–M and M* (the bands 1760 and 1650 cm^{-1}, respectively), existing at equilibrium:

$$M \rightleftharpoons M^*. \tag{2}$$

The shift of the equilibrium in the direction of the molecular form with increasing temperature is evidence that the zwitterion formed in this case is energetically more stable.

The situation changes again for another strongly polar solvent–dimethyl sulfoxide (Fig. 2c). In this case an ionic form also predominates in solution, while the band of the molecular form has a frequency of ~1725 cm^{-1}, which is evidently explained by the formation of the H-bond COOH...O=S. For this reason, the concentration of dimers is also lower than in the preceding cases. Actually, the band of the ionic form 1640 cm^{-1}

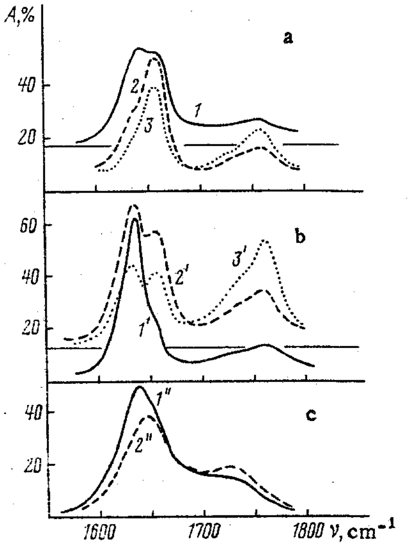


Fig. 2

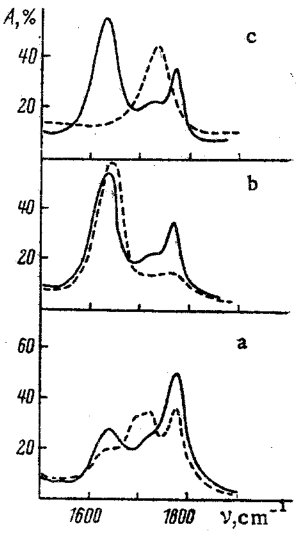


Fig. 3

Fig. 2. Spectra of solutions of DBG in CH_3CN (a), $CHCl_3$ (b), and $(CH_3)_2SO$ (c); 0.1 (1, 1'), 0.0063 (2, 3), 0.0016 (2', 3') and 0.05 M (1", 2"); T = 26 (1, 2, 1', 2', 1"), 72 (3), 50 (3') and 80°C (2").

Fig. 3. Spectra of solutions of DBG in 0.0015 (a) and 0.025 M (b, c) C_2HCl_3 (solid curves) and of the same solutions in the presence of 0.015 M $(CH_3)_2SO$ (a), 0.4 M CH_3OH (b), and 0.4 M HCl (c) (dashed curves).

changes negligibly when the solution is diluted, and, consequently, is due chiefly to absorption of the monomers M^*. Thus, in solution in $(CH_3)_2SO$ the equilibrium (2) predominates; both forms (M and M^*) are bonded to the solvent molecule by a strong hydrogen bond.

It might be thought that the appearance of a stable bipolar ion in solutions in CH_3CN and $(CH_3)_2SO$ is explained by a stabilization in a medium with electric constant ($\varepsilon = 37$ and 45, respectively). However, in solutions in alcohols, the dielectric constant of which is lower, the neutral form is absent altogether; moreover, an identical picture is observed for CH_3OH and C_2H_5OH ($\varepsilon = 32$ and 24). Moreover, the existence of the equilibrium (2) could also be recorded in solution in chloroform ($\varepsilon = 4.3$). From Fig. 2b it is evident that two bands are present in the region of absorption of the ionic form—1635 and 1650 cm^{-1}. At a concentration of $\sim 10^{-1}$ M, the second of them is masked by the more intense first. The band of the molecular monomer at 1760 cm^{-1} also has a very low intensity. With dilution of the solution, the intensity of the band 1635 cm^{-1}, belonging to D^* falls, while the intensities of the bands 1650 and 1760 cm^{-1} show a correlated increase. Just as in the case of CH_3CN, this permits an assignment of these bands to the forms M^* and M, respectively. Thus, in solutions in $CHCl_3$ and CH_3CN there is a complex equilibrium between ionic dimers and two types of monomers:

$$\begin{tikzcd} 2M^* \arrow[dd, shift left] \arrow[dr, shift left, "K_2"] & \\ & D^* \arrow[ul, shift left] \arrow[dl, shift left] \\ 2M \arrow[uu, shift left, "K_1"] \arrow[ur, shift left, "K_2'"'] & \end{tikzcd} \qquad (3)$$

Here K_1, K_2, and K_2' are equilibrium constants. Table 1 presents the values of these constants at 25°C, determined according to the intensities of the bands 1635, 1650, and 1760 cm^{-1}, and the corresponding values of the enthalpies, found according to their temperature dependence in the interval 20-60°C. The bands were separated graphically. A determination of the concentrations of various forms was performed on the assumption that the integral absorption coefficients (ε) of the bands $\nu C{=}O$ and $\nu_a CO_2^-$ do not depend on the temperature and that (ε) $\nu_a CO_2^-$ is the same in M^* and D^*, calculated per molecule. The numerical value of (ε) $\nu C{=}O$ was determined according to the spectra of DBG in CCl_4 and in C_6H_5Cl at high temperatures, when the concentration of the ionic form is negligible. We measured (ε)$\nu_a CO_2^-$ according to the spectra of alcohol solutions. The values of ΔH were determined both according to the temperature dependence of the equilibrium constants and directly according to the temperature dependence of the ratio of the intensities of the bands of the monomers and dimers.

TABLE 1. Thermodynamic Characteristics of Equilibria in a Solution of DBG in $CHCl_3$

K_1, liters/mole	K_2, liters/mole	K'_2, liters/mole	ΔH_1, kcal/mole	ΔH_2, kcal/mole	$-\Delta H'_2$, kcal/mole
$0{,}9 \pm 0{,}3$	3500 ± 1500	2400 ± 1400	$7{,}5 \pm 1$	6 ± 1	22 ± 3

The latter method does not require a knowledge of the numerical values of (ε). These data give an idea of the energetics of various structures of DBG in solution in $CHCl_3$. The value of ΔH_1 is of the same order as the enthalpy change in the transfer of a proton in the complex carboxylic acid–amine [12].

A common characteristic of alcohols and chloroform is the presence of proton donor groups XH in their molecules. In these solvents, the stable ionic form of DBG can exist by the formation of a hydrogen bond $CO_2^- \ldots HX$. In solution in $CHCl_3$, this effect leads to the appearance of a certain amount of the form M* and the establishment of equilibrium (3). In the case of alcohol, which is a stronger proton donor, the equilibrium is entirely shifted in the direction of M*. Analogous effects were observed earlier in [13, 14], devoted to the investigation of equilibria in carboxylic acid–amine systems.

Hence, it can be concluded that the structure of AA in solutions depends not only on the polar properties of the solvent, but also on the nature of the specific interactions of AA with solvent molecules. This conclusion is confirmed by experiments with ternary systems DBG + inert solvent + proton donor or acceptor (Fig. 3). Thus, as dimethyl sulfoxide is added to a solution of DBG in C_2HCl_3, the band of the molecular form 1765 cm^{-1} is weakened, and a new band 1725 cm^{-1} appears, similar to the band in the spectrum of a solution in dimethyl sulfoxide and evidently belonging to $\nu C{=}O$ of DBG in a complex with $(CH_3)_2SO$. The band of the ionic form is also weakened in this case, since the concentration of $(CH_3)_2SO$ is low ($\sim 10^{-3}$ M), and the dielectric constant of the solution is low. When CH_3OH is added, however, there is an increase in the intensity of the band of the ionic form and a decrease, and then total disappearance of the band of the molecular form (formation of a bond $CO_2^- \ldots HOCH_3$). Finally, when hydrogen chloride is added to the solution (Fig. 3c), both bands disappear, and a new band appears at 1730 cm^{-1}. In this case the HCl molecule is bonded to the nitrogen atom, while the carbonyl group remains unionized.

To determine the structure of isolated AA molecules, unperturbed by interaction with the surrounding medium, an investigation was made of the IR spectra of vapors of DBG in glycine at increased temperatures. In the case of DBG the vapor pressure was sufficient for recording the spectra with the cuvette described at the temperatures 140–150°C. From Fig. 4 it is evident that at such temperatures the band 3570 cm^{-1}, typical of the free hydroxyl group, several bands of the C_4H_9 group (in the region of 2800–3000 cm^{-1}), and two overlapping bands in the region of $\nu C{=}O$ (1720 and 1790 cm^{-1}) are present in the spectrum. When the temperature is further increased, the bands 3570, 1790, and 2800–3000 cm^{-1} show a correlated increase, while the intensity of the band 1720 cm^{-1} increases negligibly, and then evidently even decreases, which is difficult to determine exactly on account of the overlapping of the bands. The comparatively small half-widths of these bands and the absence of distinguishable traces of rotational structure confirm the fact that the bands belong precisely to DBG, and not to lighter products of its pyrolysis. The bands of such products (CO_2, CH_4, etc.) actually appear at temperatures $\sim$200°C and above; in this case the intensity of all the enumerated bands of DBG begin to decrease. The origin of the band 1720 cm^{-1} is not entirely clear. Most likely it belongs to molecular-type dimers of DBG. Analogous bands 1720 and 1800 cm^{-1} were also recorded in the case of glycine; however the density of glycine vapors is low even at the temperatures 195 to 200°C. In this case the intensity of the bands in the region of $\nu C{=}O$ is also very low, while the bands ν OH cannot be observed at all. Further increasing the temperature, just as in the case of DBG, leads to decomposition of the AA, accompanied by the appearance of the bands of NH_3, H_2O, CO_2, etc. Thus, the data obtained are evidence that in the gas phase glycine and dibutylglycine are neutral molecules. In both cases, no bands typical of ionic structures were detected. Consequently, in contrast to the results of the calculations [7], we can conclude that intramolecular transfer of a proton in an isolated AA molecule, with the formation of a zwitterion, is energetically unprofitable.

The mechanism of the formation of ionic forms of AA in the condensed phase evidently differs in different solvents. In aqueous and alcohol solutions, proton transfer occurs with the direct participation of the solvent molecules, for example, in two steps: first from the hydroxyl group to the solvent, and then from the solvent to the amino group. In the case of more inert solvent systems, however, the role of the medium in the formation of ionic forms evidently consists of a lowering of the free energy of the these forms on account of orientation and polarization of the solvent molecules, the formation of weak hydrogen bonds, etc. In the formation of

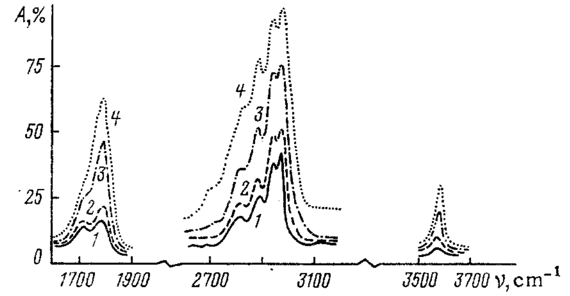


Fig. 4. Spectra of DBG vapors at T = 156 (1), 167 (2), 192 (3), and 207°C (4).

an ionic-type cyclic dimer in a nonpolar solvent, there is an intermolecular transfer of two protons along hydrogen bonds O—H...N. The formation of a zwitterion can occur either as a result of dissociation of the dimer or, which is more probable, by intramolecular proton transfer. In both cases the energetics of the process should depend substantially on the presence or absence of an intramolecular hydrogen bond in the glycine and DBG molecules. According to [8], an anomalously high value of the frequency $\nu C{=}O$ (1760-1780 cm^{-1}) in the spectra of the neutral form of α-amino acids indicates the presence of an intramolecular H-bond COOH...N (cis-form). The position of the signal of the proton of the OH group in the NMR spectrum of a solution of DBG in CCl_4 (δ = 12.2 ppm) also supports this assumption. However, in the IR spectra of DBG in the gas and in an inert solvent, as has already been noted, a band typical of the free hydroxyl group in present. Consequently, at least part of the DBG molecules are in a state without an intramolecular H-bond (gauche-form). Unfortunately, a distinct picture of equilibrium between the cis- and gauche-forms could not be observed. In the spectrum of the gas phase, no bands that might be assigned to νOH of the cis-form are observed. However, these spectra were recorded at high temperatures, when the cis-gauche-equilibrium, if it exists, might be strongly shifted in the direction of the gauche-conformer. In the case of solution in CCl_4, together with the band 3530 cm^{-1}, weak absorption is recorded in a broad region, 2700-3200 cm^{-1}. But when the temperature is varied in the interval 20-70°C, no appreciable redistribution of the intensities occurs. Expansion of the temperature interval, however, is prevented by chemical instability of CCl_4 at high temperatures. The spectrum of a solution in C_6H_6 was investigated all the way up to 200°C. In this case an increase in the band 3510 cm^{-1} could be observed, while the region 2800-3300 cm^{-1} is inaccessible on account of the absorption of the solvent. In the region of $\nu C{=}O$, in the spectra of all the solutions of DBG, together with the band 1760-1770 cm^{-1}, a shoulder is present around 1730-1740 cm^{-1} (see Figs. 1-4). However, the shoulder does not exert any distinct temperature dependence (possibly on account of overlapping with other, stronger bands), and its interpretation remains obscure. Thus, the question of an intramolecular H-bond in the neutral form of the investigated amino acids will require further study.

Hence, the data obtained permit us to draw the following conclusions. In a gas in inert solvents, free molecules (monomers) of DBG exist in the neutral form. In inert and weakly proton acceptor solvents, at a sufficient DBG concentration, dimers possessing an ionic structure may be formed. Stabilization of the zwitterion form of the monomer occurs in solvents with high dielectric constant, as well as in the presence of proton donor groups in the solvent molecules. In certain solvents an equilibrium can be observed between the molecular monomer and the zwitterion. In polar solvents, the molecules, of which possess high proton acceptor capacity, no dimer formation occurs, and there is an equilibrium between AA molecules bonded to the solvent by an H-bond and zwitterions. In aqueous and alcohol solutions, the only observable form is the zwitterion.

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ANALYSIS OF THE UV SPECTRA OF MODEL LIGNIN SUBSTANCES OF THE PHENOL SERIES

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Ultraviolet spectroscopy is one of the widely used physicochemical methods of investigating various processes in the chemistry of wood pulp and cellulose.

A series of papers [1-9] has been devoted to the problem of investigating the UV spectra of model lignin substances. However an analysis of the published data with respect to the composite absorption contours of lignin substances showed that the very same bands of the spectrum are attributed by the various authors to different parts of the molecule, a series of overlapping bands remains unmentioned, and the shortwave region of the spectra below 230-240 nm is usually not interpreted.

Although the results of the resolution of the overall absorption contours and the detection of individual bands and their identification are given in a number of papers [10-16], such an approach to the UV spectroscopy of lignin nevertheless has not found broad use in the investigation of the chemical processes.

In this paper an attempt has been made to resolve the overall absorption contours of a series of model ligin substances of a phenolic nature in the UV region of the spectrum and to interpret the individual bands obtained.

In order to attain the established goal in the spectroscopy of organic compounds various methods of depicting rounded bands with analytical functions are used employing a nonlinear approximation by least squares. At this time, Gaussian and Lorentzian shapes of the bands are used, and also their sums and other combinations. The choice of the method is made on the basis of comparing the degree of convergence of the series and according to the calculation time necessary to attain the desired result, an approximation.

The UV spectra of the model substances investigated were run in neutral and alkaline mediums on a Pie-Unicam SP-1800 spectrophotometer in the 195-400-nm region. In order to resolve the overall absorption contour into individual bands, the latter were reconstructed on the coordinates D = f (in ν, cm^{-1}). The calculations were carried out on a computer using a nonlinear approximation by the least-squares method based on the fact that the absorption distribution in the contours of the individual bands conforms to a normal Gaussian distribution. The resolution of the overall absorption contours was carried out from the long wave less loaded region assigning an orientation number to the Gaussian components and achieving convergence of the calculated contours with the experimental one not exceeding 5%. Otherwise an additional correction to the number of Gaussian components and their half-widths was carried out. The contours were checked by subjecting them to the equation

$$D_i = D_{\max} \exp\left[-\frac{4(\nu_i - \nu_{\max})^2}{\sigma^2} \right] \ln 2, \tag{1}$$

where D_i, $D_{\max}$ is the absorption for the i-th frequency or the frequency of the maximum; ν_i, $\nu_{\max}$ is the i-th frequency or frequency of the maximum; σ is the half-width of the absorption.

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