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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

CHEMISTRY

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ON THE QUESTION OF THE TAUTOMERISM OF AMIDES

It is generally known that tautomerism may occur in amides of carboxylic acids,

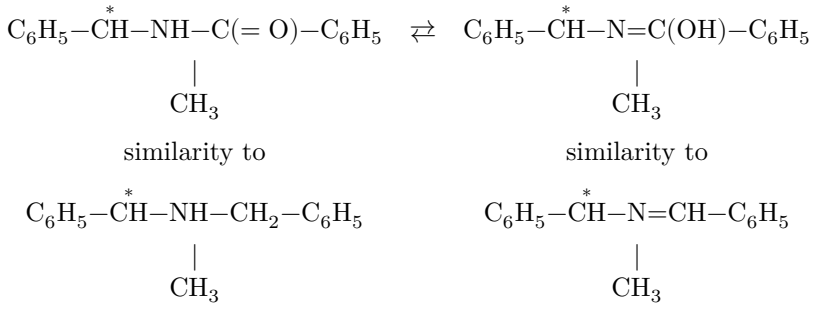
$R-\mathrm{CONH_2} \rightleftarrows R-\mathrm{C(OH)}{=}\mathrm{NH}.$

Although various investigators have employed both chemical and physical methods (refractometry, ultraviolet and infrared spectra, dipole moments, Raman spectra), there is still no unified opinion on the question of the structure of amides. In this connection we may cite, for example, the directly opposite conclusions of Hantzsch ([1]) and of Grob and Fischer ([2]). Nor, in any case, have the two forms of amides yet been actually isolated.

Fig. 1

Investigating, with the aid of a simple variant of a photoelectric spectropolarimeter constructed in our laboratory, the rotatory-dispersion curves of certain derivatives of optically active α-phenylethylamine in the ultraviolet region of the spectrum, we obtained new data on the question of amide tautomerism.

For free α-phenylethylamine (I), N-benzyl-α-phenylethylamine (II), and benzylidene-α-phenylethylamine (III), the rotatory-dispersion curves change little on going from benzene solutions to methanolic ones. In contrast, for N-benzoyl-α-phenylethylamine (IV) the sign of rotation and the course of the dispersion curve in benzene (italic lines) and in methanol (solid lines) are directly opposite (Fig. 1): in benzene IV shows similarity to II, and in methanol to III; i.e., apparently, in benzene the lactam form predominates, and in methanol the lactim form predominates (cf. the data of Yu. N. Sheinker on amino derivatives of pyridine and thiazole ([3])).



In agreement with this interpretation, the benzoyl derivative of amine II does not exhibit such a solvent effect (Fig. 1, V), since there is no H atom on the nitrogen capable of tautomeric transition.

The data obtained compelled us to carefully recheck the information available in the literature on the difference in the melting points of benzoyl-α-phenylethylamine: 122° from alcohol and 125° from ligroin ([4], [5]). It turned out that if a preparation recrystallized from heptane, with m.p. 128-129°, is heated for some time in dilute methanol, then on cooling a form separates from the solution with m.p. 123°. Observing the melting process under a microscope, one can see how the substance that has melted at 123°, despite a slow rise in temperature, solidifies again and then melts again at 128°. Apparently, this is the first observation here of the transition of two tautomeric forms—the labile lactim form (m.p. 123°) into the stable lactam form (m.p. 128°).

The spectropolarimetric method will undoubtedly prove to be an interesting means of studying other cases of tautomerism as well. At present we are continuing the study of the behavior of amides, as well as of compounds of the aminocrotonic ester type.

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Note: Figure translations are in progress. See original paper for figures.