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Fig. 1. UV absorption spectra. A −(−) α-phenylethylamide of picolinic acid; B −(−) α-phenylethylamide of nicotinic acid; C −(−) α-phenylethylamide of isonicotinic acid

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Abstract

Full Text

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SPECTROPOLARIMETRIC BEHAVIOR OF α-PHENYLETHYLAMIDES OF PYRIDINECARBOXYLIC ACIDS

In studying the dispersion of optical rotation of α-phenylethylamides of para-substituted benzoic acids, V. M. Potapov and A. P. Terent' ev ([1], [2]) found that, depending on the polarity of the solvent, the rotation-dispersion curve (RD curve) follows different courses; this was explained as a consequence of amide-iminol tautomerism. Subsequent spectropolarimetric studies showed that the difference in the behavior of such amides is determined not by tautomerism but, apparently, by a difference in the mesomeric states of the amide group ([3], [4]). The works of Skul' skii ([5], [6]) confirmed the presence of the effect described above. On the basis of a study of NMR spectra, he came to the conclusion that amide–iminol tautomerism is absent and expressed the opinion that the cause of such behavior of the amides may be the formation of solvates or comparatively stable conformations.

Fig. 1. UV absorption spectra. **A** −(−) α-phenylethylamide of picolinic acid; **B** −(−) α-phenylethylamide of nicotinic acid; **C** −(−) α-phenylethylamide of isonicotinic acid.

In the present work we investigated the spectropolarimetric behavior of amides of pyridinecarboxylic acids that differ in the position of the carboxamide group in the pyridine ring. As the optically active substance ("optically active indicator"), as in a number of preceding works ([1–4]), (−)-α-phenylethylamine was used. UV spectra were recorded and RD curves were measured for α-phenylethylamides of α-, β-, and γ-pyridinecarboxylic acids. The UV spectra of

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Fig. 2. Dispersion of molecular optical rotation of (−)α-phenylethylamides: 1 −picolinic, 2−nicotinic, 3−isonicotinic, 4−5-ethylpicolinic, 5−6-methylpicolinic, 6−2-methylisonicotinic acids. a−in methanol, b−in benzene, c−in dioxane

Figure 2: Fig. 2. Dispersion of molecular optical rotation of (−)α-phenylethylamides: 1−picolinic, 2−nicotinic, 3−isonicotinic, 4−5-ethylpicolinic, 5−6-methylpicolinic, 6−2-methylisonicotinic acids. a−in methanol, b−in benzene, c−in dioxane

the amides obtained differ little from one another (Fig. 1); they do not reflect structural features, whereas the spectropolarimetric behavior of these amides is substantially different.

The amide of α-pyridinecarboxylic (picolinic) acid gives RD curves whose course and sign are opposite to those for the starting amine and do not change under the influence of the solvent (Fig. 2). In the case of the amide of γ-pyri-

for pyridinedicarboxylic (isonicotinic) acid, the sign of rotation and the course of the RD curves remain the same as for the starting amine and likewise do not depend on the solvent (Fig. 2).

For the amide of β-pyridinecarboxylic (nicotinic) acid in methanol, the course of the RD curve is opposite to the course of the RD curve of the starting amine, whereas in benzene the course of the curve and the sign of rotation are the same as for the starting amine.

Using as examples the phenylethylamides of 5-ethylpicolinic, 6-methylpicolinic, and 2-methylisonicotinic acids, it is seen that introduction of alkyl substituents into the pyridine ring does not affect the sign and course of the RD curves, but increases the magnitude of rotation (see Fig. 2), which is more likely associated with an increase in the volume of the radical than with the +/− effect of the alkyl groups. This gives a substantial advantage in comparison with absorption spectra in the UV region.

Comparison of the behavior of the amides of pyridinecarboxylic acids indicates that the amide of nicotinic acid behaves similarly to the corresponding benzamide ([1,2]). In the case of the amide of picolinic acid, apparently, greater importance is attached to the ability to form an intramolecular hydrogen bond, which leads to a strong change in the structure of the substituent. The data obtained are not sufficient for their unambiguous interpretation; however, it is already clear that the phenomenon we have discovered−the sharply different spectropolarimetric behavior of the amides of pyridinecarboxylic acids, which differ only in the relative position of the carbamide group−may become an effective method for establishing the structure of organic compounds and determining them in mixtures.

Fig. 2. Dispersion of molecular optical rotation of (−)α-phenylethylamides: 1 −picolinic, 2−nicotinic, 3−isonicotinic, 4−5-ethylpicolinic, 5−6-methylpicolinic,

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6—2-methylisonicotinic acids. *a*—in methanol, *b*—in benzene, *c*—in dioxane.

Experimental Part

Phenylethylamide of picolinic acid. A mixture of 2 g of methyl ester of picolinic acid (b.p. 122-123°/12 mm), 2.2 g of (−)α-phenylethylamine ($[\alpha]_D$ − 40.8°), and 1 drop of H_2SO_4 was boiled for 4-5 h. After cooling, the solidified mixture was recrystallized three times from heptane. Obtained: 2.6 g (63%) of α-phenylethylamide, m.p. 55°, Rf*0.71.

* Everywhere the Rf values are given as obtained by thin-layer chromatography on a nonfixed layer of aluminum oxide of activity grade II in the system benzene:methanol = 25:1.

Table 1

(−) α-Phenylethylamides of acids	M.p., °C	Rf	$(M)^{20}_{436}$ in CH_3OH	Formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	UV spectrum (in methanol), λ_{max}	UV spectrum (in methanol), lg ε
2-Pyridinecarboxylic (picolinic)	55	0.61	+48.15°	$C_{14}H_{14}N_2O$	74.08	6.23	74.33	6.16	266	3.76
3-Pyridinecarboxylic (nicotinic)	82	0.40	+4.64°	$C_{14}H_{14}N_2O$	74.10	6.25	74.33	6.16	238	4.36
4-Pyridinecarboxylic (isonicotinic)	102	0.22	−76.16°	$C_{14}H_{14}N_2O$	74.40	6.27	74.33	6.16	250	3.7
5-Ethyl-2-pyridinecarboxylic	64	0.78	+244.03°	$C_{16}H_{18}N_2O$	75.35	7.08	75.59	7.09	268	4.0
6-Methyl-2-pyridinecarboxylic	b.p. 175-176/1 mm	0.73	+201.48°	$C_{15}H_{16}N_2O$	75.20	6.82	75.00	6.66	268	3.8

(−) α-Phenylethylamides of acids	M.p., °C	Rf	$(M)_{436}^{20}$ in CH_3OH	Formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	UV spectrum (in methanol), λ_{max}	UV spectrum (in methanol), lg ε
2-Methyl-4-pyridinecarboxylic	130	0.45	−28.2°	$C_{15}H_{16}N_2O$	–		75.00	6.66	250	2.21

Phenylethylamides of other pyridinecarboxylic acids were synthesized analogously (Table 1).

To obtain the phenylethylamide of nicotinic acid, to 1.3 g of the chlorohydrate of nicotinic acid chloride (7) was added a threefold excess (2.68 g) of (−)α-phenylethylamine in 17 ml of chloroform; the mixture was boiled on a water bath for 2 hours. After cooling, it was shaken in a separatory funnel with a small amount of water; the chloroform layer was separated, the chloroform was distilled off, and the residue was recrystallized from a mixture of heptane and hexane. Yield of amide 1.2 g (72%), m.p. 82°.

The ORD curves were measured with the aid of a domestic spectropolarimeter of VNIIKIProdmash. The concentration of the measured solutions was 1.5-1.7% (0.08-0.09 M).

Amides were synthesized from optically active α-phenylethylamine and pyridinecarboxylic acids. A spectropolarimetric study of these amides showed that the course of the ORD curves depends on the position of the carboxyl group in the pyridine ring. In the case of the amide of nicotinic acid, an effect of the solvent on the character of the ORD curves was noted.

Introduction of alkyl substituents has no effect on the sign or course of the ORD curves, but increases the rotation.

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