RING-CHAIN ISOMERISM OF o-CYANOBENZAMIDE

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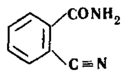
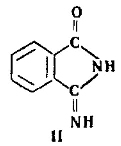
UDC 547.756:542.952.1:543.422.4

Braun [1] was the first to observe that o-cyanobenzamide (I), after melting at 172-173°C, solidifies and again melts at 200°. This was explained by thermal isomerization (I→II). The isomerization of I to II was also accomplished under basic catalysis conditions, and phthalimide monoimine (II) with mp 203° was obtained; II is readily hydrolyzed to phthalimide.



I



II

We have observed [2] double melting points for several γ-ketoamides. It has been demonstrated [2, 3] that thermal isomerization of the chain form to the open form (hydroxylactam→ketoamide) is realizable in the case of several γ-ketoamides and o-acylbenzamides. The reverse direction of the thermal ring-chain isomerization of o-cyanobenzamide to an iminolactam can be explained by extremely approximate calculations of the energy of formation of I and II. Proceeding from the averaged energies of formation of the bonds [4], it can be shown that $E_{II} > E_{I}$. In the case of γ-ketoamides, on the other hand, $E_{\text{ketoamide}} > E_{\text{hydroxylactam}}$.

The IR spectra of I and II were studied in order to obtain a more distinct proof of the structures of I and II and to ascertain whether I and II are stable isomers or whether the equilibrium $I \rightleftharpoons II$ occurs in solutions.

Flett [5] has observed unusually high (for benzamides) $\nu_{C=O}$ frequencies (amide I band) at 1753 cm^{-1} and δ_{NH_2} frequencies (amide II band) at 1667 cm^{-1} in the IR spectrum of o-cyanobenzamide (KBr pellet) and explains this by hindrance to association on the part of the bulky nitrile group. These results, which are characterized as anomalously high for $\nu_{C=O}$ and δ_{NH_2} of amides, are also presented in a monograph by Bellamy [6]. It is curious that Flett did not observe a band at 1400 cm^{-1}, which is characteristic for a large set of other primary amides, in his spectrum of o-cyanobenzamide (the physical constants of the compound are not presented in [5].)

In a study of the IR spectra* of I and II, obtained by the method in [1], it was found that the IR spectrum of I does not correspond to Flett's data [5]. The spectrum of I (KRr pellet) contains $\nu_{C=O}$ 1658, δ_{NH_2} 1626, aromatic ring $\nu_{C\equiv N}$ 1593, 1574, and 1496 cm^{-1}; an intense band is observed at 1399; ν_{N-H} 3352 and 3175; $\nu_{C=C}$ 2235 cm^{-1}. In dioxane, $\nu_{C=O}$ is 1692 cm^{-1} (A = 3.83 practical units), and δ_{NH_2} is 1614 cm^{-1}, compared with 1687 and 1626 cm^{-1} in dimethyl sulfoxide, and 1694 and 1612 cm^{-1} in acetonitrile. These results confirm structure I and differ only slightly from the results of an investigation of other benzamides [5]. A complex absorption pattern is observed in the spectrum of crystalline II (KBr pellet) at 1500-1800 cm^{-1}: 1723, 1696 (shoulder), 1674, 1613, 1595, and 1537 cm^{-1}. The presence of several high-frequency bands is apparently due to strong intermolecular C = O...H–N hydrogen bonds in the

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* The spectra were recorded with an IKS-14 spectrometer. The solution concentration was $2.5 \cdot 10^{-2}$ M. The integral intensities (A) were calculated by the Wilson–Wells method with Ramsay's corrections for the "wings" and are given in practical units of measurement of 10^4 liter · mole^{-1} · cm^{-2}.

Riga Polytechnic Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 281-282, February, 1972. Original article submitted May 12, 1971.

crystal lattice. In solutions, there are two intense bands in this range: $\nu_{C=O}$ 1737 (A=4.57) and $\nu_{C=N}$ 1671 cm^{-1} (A=3.04) in dioxane, 1733 and 1667 cm^{-1} in dimethyl sulfoxide, and 1743 and 1674 cm^{-1} in acetonitrile. It was found that I and II are stable in dioxane, dimethyl sulfoxide, and acetonitrile and do not form an equilibrium mixture ($I \rightleftharpoons II$) at room temperature.

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