TAUTOMERISM AND GEOMETRIC ISOMERISM OF NITROGEN-CONTAINING DERIVATIVES OF CARBONYL COMPOUNDS
COMMUNICATION 7. ULTRAVIOLET SPECTRA OF SOME SEMICARBAZONES AND THIOSEMICARBAZONES

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In the study of the polarographic behavior and structure of semicarbazones and thiosemicarbazones of aldehydes and ketones [1-3] the necessity arose of comparing results obtained by means of polarography with the results of other physicochemical methods. The interesting question of the structure of semicarbazones and thiosemicarbazones has been discussed several times in the literature, mainly on spectrographic evidence. Some information on the ultraviolet spectra of semicarbazones and thiosemicarbazones may be found in Gillam and Stem’s monograph[4]. In a study of the effect of pH on the position of the maximum in the absorption spectrum of p-nitrobenzaldehyde semicarbazones Cilento [5] observed a bathochromic shift in the maximum of 5 mμ on transition to alkaline solutions, and this he attributed to the formation of a quinonoid structure under these conditions. We did not succeed in detecting polarographically the formation of a quinonoid structure in p-nitrobenzaldehyde derivatives in alkaline solutions, though these compounds dissolved in alkalis with formation of yellow solutions [3]. It is probable that in alkaline solutions the reduction of the nitro group occurs at the same potential as that at which the quinonoid structure of p-nitrobenzaldehyde derivatives must be reduced. We therefore decided to study semicarbazones and thiosemicarbazones of various aldehydes and ketones by the method of ultraviolet spectroscopy as being more sensitive to changes in the electronic structure of molecules under conditions close to those of polarography [1, 3].

EXPERIMENTAL

Determinations were made of the ultraviolet spectra of aqueous-alcoholic solutions of semicarbazones and thiosemicarbazones of the isomeric nitrobenzaldehydes and of p-dimethylaminobenzaldehyde at different pH values. In addition, a study was made of the effect of the nature of the solvent on the position of the maximum for the absorption spectra of the thiosemicarbazones of benzaldehyde, acetophenone, cyclohexanone, acetone, and their methylation products, and also of the 4,4-dimethylthiosemicarbazone of cyclohexanone. The ultraviolet spectra of solutions of semicarbazones and thiosemicarbazones were determined on an SF-4 spectrophotometer at room temperature.

All the substances investigated in this work were synthesized by methods described in the literature.

Spectra of Derivatives of the Isomeric Nitrobenzaldehydes and of p-Dimethylaminobenzaldehyde. The ultraviolet spectra of semicarbazones and thiosemicarbazones of the isomeric nitrobenzaldehydes and of p-dimethylaminobenzaldehyde in 40% alcoholic-aqueous neutral solutions are characterized by an intense absorption band in the region 270-357 mμ (Table 1).

As will be seen from Table 1, the wavelength at the absorption maximum is shifted toward the long waves on transition from semicarbazones to the corresponding thio analogs, which is in accord with the relative strengths of the chromophores C=O and C=S [4]. It follows from Table 1 that the position of the substituent in the benzene ring has a substantial effect on the shift in λ_max: the extent of the bathochromic shift increases as we pass from the o-nitro to the p-nitro derivative. This is in accord with Hinman’s results [6] for the semicarbazones of m- and p-nitrobenzaldehydes. The large nitro group in the ortho position interacts sterically with the azomethine grouping, leading to disruption of its coplanarity with the benzene ring. As a result, the participation of the o-nitro group in the conjugation is reduced; it is this that determines the hypsochromic shift in λ_max for o-nitro derivatives.
Table 1 shows that for the semicarbazones and thiosemicarbazones of m- and o-nitrobenzaldehydes the effect of the pH of the solution on the position of $\lambda_{\text{max}}$ is very slight. This indicates that the structures of these compounds in solution do not undergo substantial change with change in pH. For the p-nitrobenzaldehyde derivatives, however, the position of $\lambda_{\text{max}}$ depends greatly on the concentration of hydrogen ions in the solution. Thus, for p-nitrobenzaldehyde thiosemicarbazone there is a shift in $\lambda_{\text{max}}$ by 15 m$\mu$ for an increase in the pH of the solution from 10.1 to 11.4. At the same time the solution acquires a yellow color. Such a bathochromic displacement of $\lambda_{\text{max}}$ for p-nitrobenzaldehyde derivatives is clearly to be explained by the formation of a quinonoid structure:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} = \text{C} = \text{N} - \text{NH} = \text{C} - \text{NH}_2
\end{array}
\]

The absorption spectra of the thiosemicarbazones of m- and p-nitrobenzaldehydes, determined at different pH values, are given in Fig. 1.

For o-nitrobenzaldehyde derivatives, in which the o-nitro group is not coplanar with the benzene ring, such a transformation in alkaline is impossible, which is confirmed by experiment.

Freshly prepared weakly acid solutions of p-dimethylaminobenzaldehyde derivatives have a yellow color, which disappears in the course of time. The ultraviolet absorption spectra of these solutions are characterized by two intense absorption bands, whereas neutral solutions of the semicarbazone and thiosemicarbazone of p-dimethylaminobenzaldehyde give one absorption band in this region of the spectrum. Thus, an acid solution (pH 2.0) of p-dimethylaminobenzaldehyde semicarbazone gives absorption bands with maxima at 285 and 352 m$\mu$ (Fig. 2); for the thio analog of this compound under the same conditions the maxima are at 310 and about 360 m$\mu$ (Fig. 3) (the longer-wave maximum is not very distinct). This notable difference in the absorption spectra of neutral and acid solutions of p-dimethylaminobenzaldehyde derivatives is probably determined by the formation of a structure with a quaternary nitrogen:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} = \text{C} = \text{N} - \text{N} = \text{C} - \text{NH}_2
\end{array}
\]