Monatshefte für Chemie 118, 669—670 (1987)

Monatshefte für Chemie
Chemical Monthly

Tautomerism of 2-(*o*-Hydroxyphenyl)-Azines

Short Communication

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(Received 7 December 1986. Accepted 2 January 1987)

The tautomeric properties of *o*-hydroxyphenylazines have been investigated by ^{17}O NMR and UV spectroscopy. 2-(*o*-Hydroxyphenyl)-pyridine and its *p*-nitrophenole analog II exist in chloroform or ethanol as a phenol A. In the case of 2-(2-hydroxy-5-nitrophenyl)-quinoline the NH-tautomer is realized, the content of which increases when going to the dinitro-analog IV.

(Keywords: Azine tautomerism; o-Hydroxyphenylazines; ^{17}O *NMR)*

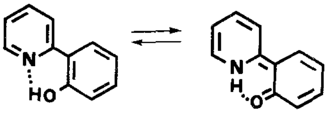
Die Tautomerie von 2-(o-Hydroxyphenyl)-azinen (Kurze Mitteilung)

Es wurden die tautomeren Eigenschaften von *o*-Hydroxyphenylazinen mittels ^{17}O-NMR und UV-Spektroskopie untersucht. 2-(*o*-Hydroxyphenyl)-pyridin und sein *p*-Nitrophenol-Analog II existieren in Chloroform und Ethanol als Phenol A. Das 2-(2-Hydroxy-5-nitrophenyl)-chinolin liegt als NH-Tautomer vor, dessen Anteil im Dinitro-Analog IV noch steigt.

Hydroxyphenylazines reveal complexing and lightstabilizing properties [1, 2]. The possibility of their tautomerism $A \rightleftharpoons B$ has been discussed repeatedly. For the first time such a possibility had been proposed by *Chichibabin* in 1918 [3]. *Abramovich* [4], on the base of IR spectra in KBr considered the nitrophenole II to have zwitterionic structure (which is, as can be seen, only another representation of the same NH tautomeric form by resonance symbolism).

While studying the compounds I–IV by UV and ^{17}O NMR spectroscopy, we have found cases of a tautomeric equilibrium of type $A \rightleftharpoons B$ in solution, on which reliable data are absent in the literature. For the hydroxyphenylpyridine I only form A is realized ($CHCl_3$, $\lambda_{max} = 320$ nm, $\delta_{OH} = 97$ ppm, cr. [5]). We could not reveal the NH-form II B also for the nitro-derivatives II in $CHCl_3$, acetonitrile or ethanole ($\lambda_{max} = 315$–

325 nm, cr. [4]). The quinoline derivative III has a characteristic absorption of the NH-form [6] ($CHCl_3$, 440 nm, shoulder), which is in accordance with the better ability of quinoline compounds to adopt the ylidene form as compared to pyridine compounds [7]. The higher intensity of the long wave absorbance (440 nm) for the dinitro-derivatives IV reflects further stabilization of the NH form with the increase of acidity of the phenolic moiety. Another reliable evidence for the tautomeric equilibrium IV A$\rightleftharpoons$IV B is a regular and reversible change of this absorbance witz the solvent used. Thus, the addition of the more polar acetonitrile to a $CHCl_3$ solution of IV increased the long wave absorption while heptane decreased it. The destabilizing effect of nonpolar solvents on the tautomers of NH type is well known [6].



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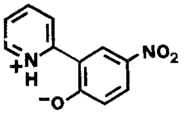

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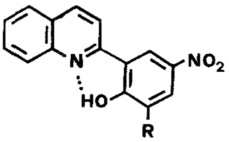

III: R=H

IV: R=NO_2

Experimental

o-Hydroxyphenylpyridines I and II were synthesized as described in the literature [3, 4]. The synthesis of the quinoline derivatives III and IV will be published elsewhere. UV spectra were recorded on a UV-VIS Specord instrument, ^{17}O NMR spectra on a Bruker CXP-300 instrument (with H_2O as a standard).

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Verleger: Springer-Verlag KG, Mölkerbastei 5, A-1010 Wien. — Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. — Redaktion: Währinger Straße 38, A-1090 Wien. — Hersteller: Adolf Holzhausens Nachfolger, Kandlgasse 19-21, A-1070 Wien. — Verlagsort: Wien. — Herstellungsort: Wien. — Printed in Austria.