ANTIPIRIN C AND ITS COMPLEXES WITH LANTHANUM

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ANNOTATION

This scientific article discusses the results of a study of the structure of antipyrine C and its lanthanum complexes. On the basis of the calculations, comparative calculated values of the maximum absorption range of the most probable structures with the experimental electronic absorption spectra of Gauss are presented, and preliminary observations of the forms of complexes under the influence of the pH of the medium are described.

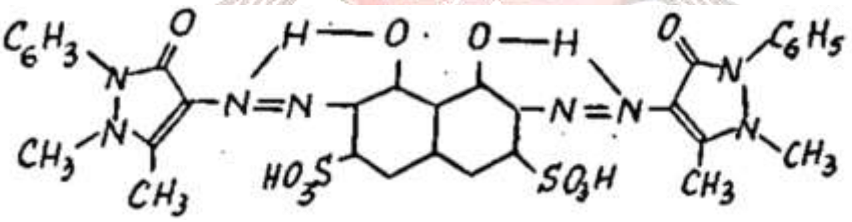
Key words: antipyrine C, absorption band, quinone hydrazone form, reagent azo form, sandwich structure, spectrum shift, quinone hydrazone tautomerism.

INTRODUCTION

Ionic states in solutions of 2,7-bis (1-phenyl-2,3-dimethyl-4-azopyrazolone-5) -1,8-dioxynaphthalene-3,6-disulfonic acid (antipyrine C) and the mechanism of its complexation with lanthanum. The choice of the most probable structures was carried out by comparing the calculated values of the absorption band maxima of possible structures with the experimental electronic absorption spectra, decomposed into individual Gaussian components, and comparing other quantum-chemical characteristics of these structures.

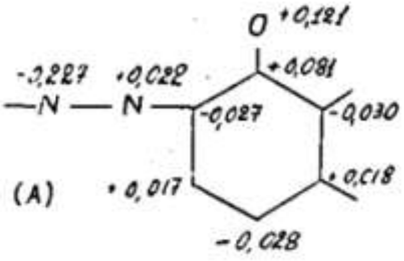
RESULTS AND THEIR DISCUSSION

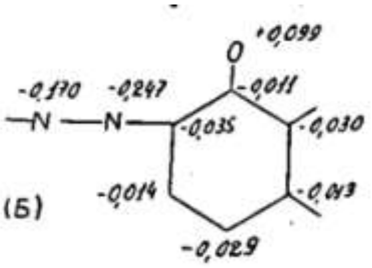
Our studies show that in media with pH = 5 - 7, the reagent is in azo form I. The quinone hydrazone form is not detected under these conditions:



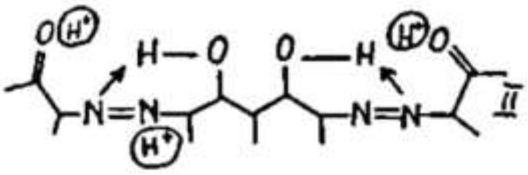
I

The features of the charge distribution in the azo form, apparently caused by strong electron-donating effects of antipyrine nuclei, are large negative charges on the nitrogen atoms of the azo groups closest to the naphthalene nucleus and the presence of negative charges on all carbon atoms of the naphthalene nucleus. This distinguishes antipyrine C from mono- and bisazo derivatives obtained by azo coupling of chromotropic acid with amino derivatives of benzene, where large negative charges are carried by the nitrogen atoms of the azo groups closest to the benzene nuclei, and the charges on the carbon atoms of the naphthalene ring alternate. This is illustrated by the following fragments of the molecular diagrams of benzene C (A) and antipyrine C (B):



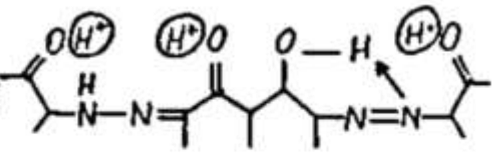


At pH = 1 - 2, a slight bathochromic shift of the spectrum is observed, which is apparently associated with the protonization of the carbonyl oxygen atom of the azo form antipyrine nucleus. With a further increase in acidity (50% H_2SO_4 solution), the absorption spectrum shifts hypsochromically, which is probably caused by the appearance of the reagent azo form protonated at both carbonyl groups. The absorption spectrum in concentrated H_2SO_4 is shifted bathochromically relative to the spectrum of the reagent at pH = 5 - 7, which may be associated with the formation of structures II and III:



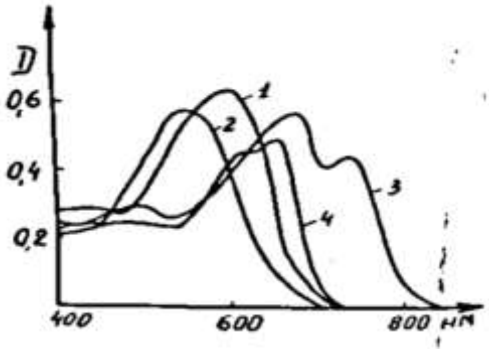
II

III



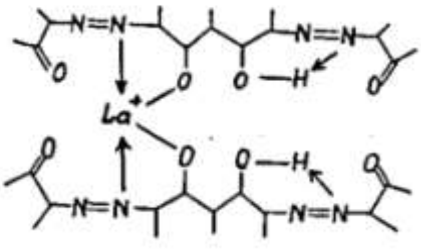
At pH 11-13, one of the hydroxy groups of the naphthalene nucleus dissociates, which causes a hypsochromic shift in the spectrum. In a 20 - 40% alkali solution, the second oxy group dissociates, which leads to a bathochromic shift of the absorption spectrum of the reagent.

Depending on the condition, the complexation of lanthanum with antipyrine C is characterized by two types of spectral curves (Fig. 1). At pH = 6.5, a complex of the composition Me: R = 1: 2 is formed with peaks in the spectrum at 610 and 650 nm. The absorption spectrum at pH = 2.5 is characterized by an additional maximum at 735 nm. The composition of the complex under these conditions is Me: R = 1: 4.

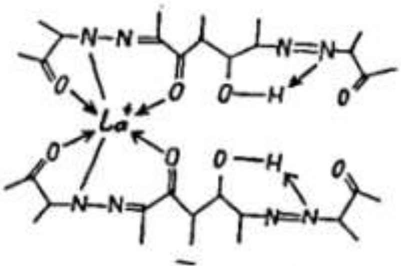


Pic. 1. Absorption spectra of antipyrine C (1-pH = 2.5; 2-pH = 6.5) and complexes with lanthanum (3-pH = 2.5; 4-pH = 6.5)

First of all, we note that, as follows from the above fragments of the molecular diagrams, as well as from the calculation data for the positions λ_{max}, the coordination of the metal to the nitrogen atom of the azo group closest to the naphthalene poison turns out to be more probable. The best agreement between the calculated and experimental data for pH = 6.5 is observed for the sandwich structure IV.



IV



V

Conclusion: an additional long-wavelength maximum in the absorption spectrum of the complex at pH = 2.5 indicates the probable formation under these conditions of complex V with the quinone hydrazone tautomer of antipyrine C, which is in equilibrium with form IV. The proposed scheme explains the spectrum of the complex at pH = 2.5, but does not explain the composition Me: R = 1: 4. Since the spectrum of the complex at pH = 2.5 also exhibits absorption in the range 550 - 600 nm, where, according to calculations, it also absorbs the azo form of the reagent, it can be assumed that this composition is associated with the phenomena of association, a possible cause of which may be the above negative charge of naphthalene. cycle of antipyrine C.

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