UDC 543.422 + 547.836

ULTRAVIOLET SPECTRA OF 2-PHENYL-4- AND 2-PHENYL-5-AZAINDAN-1, 3-DIONES

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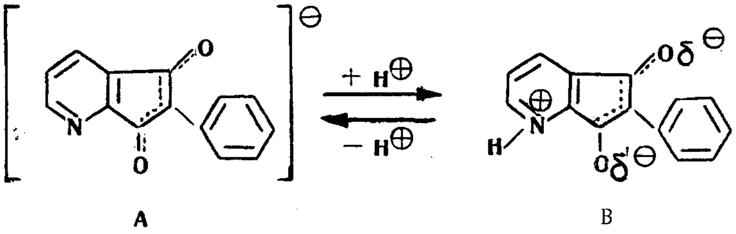
Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 93-98, 1965

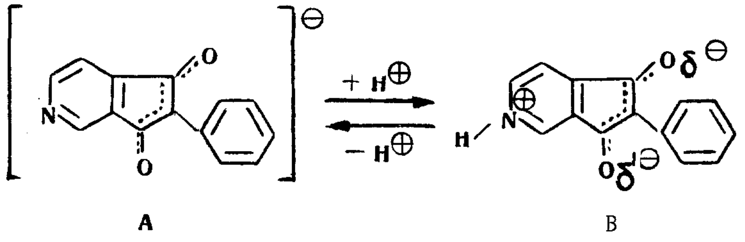
The UV spectra of 2-phenyl-4-azaindan-1, 3-dione (I), 2-phenyl-5-azaindan-1, 3-dione (II), and their N-methylbetaines are investigated. 2×10^{-5} M aqueous alcoholic solutions of 2-phenyl-4-azaindan-1, 3-dione (I) contain the anionic form (IA), and in solutions of 2-phenyl-5-azaindan-1, 3-dione (II) the betaine form (IIB) is also in equilibrium with the anion (IIA). Solutions of I and II in 0.1 M sulfuric acid are characterized by a wide and rather intense absorption band at about 500 mμ, indicating the presence of a betaine form (IB and IIB). In 2M hydrochloric acid solution 2-phenylazaindan-1, 3-diones and their N-methylbetaines (III and IV) are protonated at the oxygen atom, giving the enol forms of the N-protonated or corresponding N-methylated 2-phenylazaindandiones.

Replacement of one of the CH groups of the benzene ring in the indan-1, 3-dione molecule by a nitrogen atom manifestly alters its physical and chemical properties. In particular, the azaindandiones differ from their carbocyclic analogs by their deeper color, sometimes by greater solubility in water, and by the absence of a definite melting point; moreover, they gradually decompose when heated above 250-350° [1-3]. These peculiarities are undoubtedly connected with the unusual structure of the nitrogen analog of the indandione, and an attempt has been made to elucidate them using electronic absorption spectra. In this connection a closer study was made of the isomeric 2-phenyl-4-azaindan-1, 3-dione (I) and 2-phenyl-5-azaindan-1, 3-dione (II), analogs of 2-phenylindan-1, 3-dione (III) which has been studied in detail spectroscopically [4-7]. The UV spectra of I and II were dtermined with an SF-4 spectrometer, over the range 220-700 mμ, using 2×10^{-5} M solutions in 50 vol % ethanol, and also over the 400-700 mμ range for 2×10^{-4} M solutions.

Whereas III is known to have a characteristic tautomeric structure and may exist in solution as a diketone, enol or anion, we did not succeed in proving that I and II have diketone and enol forms. We assume that in the investigated solutions of 2-phenylazaindandiones I and II that there is equilibrium between an anion form A and a betaine form B.



I



II

However, there are also important differences between the absorption spectra of I and II. The almost identical absorption curves of a 2×10^{-5} M aqueous alcoholic solution of I and its solution in aqueous alcoholic alkalies (Fig. 1), as well as the identical yellow color of these solutions due to absorption at 456 mμ, indicates that at the concentration used I is fully dissociated. Under similar conditions the solution of II and its potassium salt (Fig. 2) have a quite similar absorption over the range 240-510 mμ, but beyond that they differ appreciably. If the yellow alkaline solution has the absorption maximum at 466 mμ (ε 1855) characteristic of the anion, in the spectrum of the reddish-violet solution of II a diffuse band with λ_{max} 475 mμ (ε 2300) is observed, the intensity of absorption beyond the 500 mμ limit decreasing rather less sharply than for the long-wavelength maximum of the alkaline solution. Evidently, the bathochromic and hypsochromic effects are connected with the betaine form (IIB), which absorbs at longer wavelengths and in this case is in equilibrium with the anion (IIA). The standard compounds used for determining betaine form absorption were N-methylbetaines of 2-phenylazaindan-1, 3-diones, made by alkylating I and II with dimethyl sulfate in an alkaline medium.

In the long wavelength region the 2×10^{-5} M violet solution of the N-methylbetaine of 2-phenyl-5-azaindan-1, 3-dione (IV) has an absorption maximum at 536 mμ (ε 2020) (Fig. 3). In the same region the spectrum of the N-methylbetaine of 2-phenyl-4-azaindan-1, 3-dione (V) is more complex, there being a wide absorption band with a marked maximum at 411 mμ (ε 11,400) and a flat bend in the range 486-570 mμ (ε 3600-1625) (Fig. 4).

When solutions of I and II are acidified (0.1 M H_2SO_4 — 50% ethanol), they give absorption curves which are very similar (Figs. 1 and 2) in shape to those for the N-methylbetaines IV and V, but less intense. The deepening of the color on acidification can also be observed visually. From what was said above it follows that 0.1 M sulfuric acid facilitates protonation of the nitrogen atom, i.e., formation of a betaine form (B). However, any of the betaines can be regarded as the anion of an azaindandione protonated or methylated at the nitrogen atom. It is evident that the differing absorption of the anions containing a pyridine (IA, IIA) and a pyridinium ring (IB, IIB, IV, V) is connected with the different electron density distribution in these systems. It is assumed that in the pyridinium compounds the electron density of the nodal carbon atoms is increased and approximates that for a double bond. In this respect betaines can be compared with the anions of 2-phenyl-4, 5, 6, 7-tetrahydroindandione and 2, 4, 5-triphenylcyclopent-4-ene-1, 3-dione, which also absorb at 520-530 mμ (ε 900-300) [8].

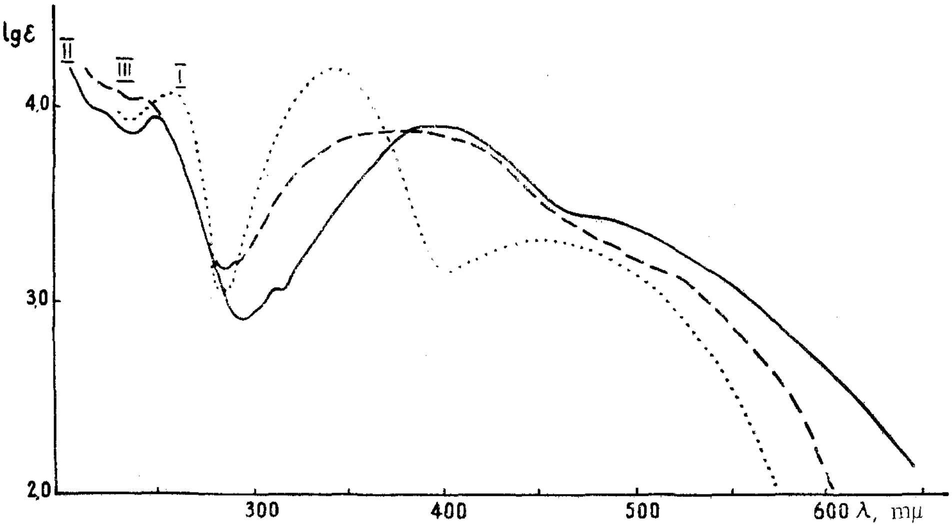


Fig. 1. UV spectra of 2 × 10^{-5} M solutions of 2-phenyl-4-azaindan-1, 3-diones in 50 vol % ethanol containing:
I - 2 mole/l KOH(IA); II - 0.1 mole/l H_2SO_4 (IB); III - 2 mole/l HCl

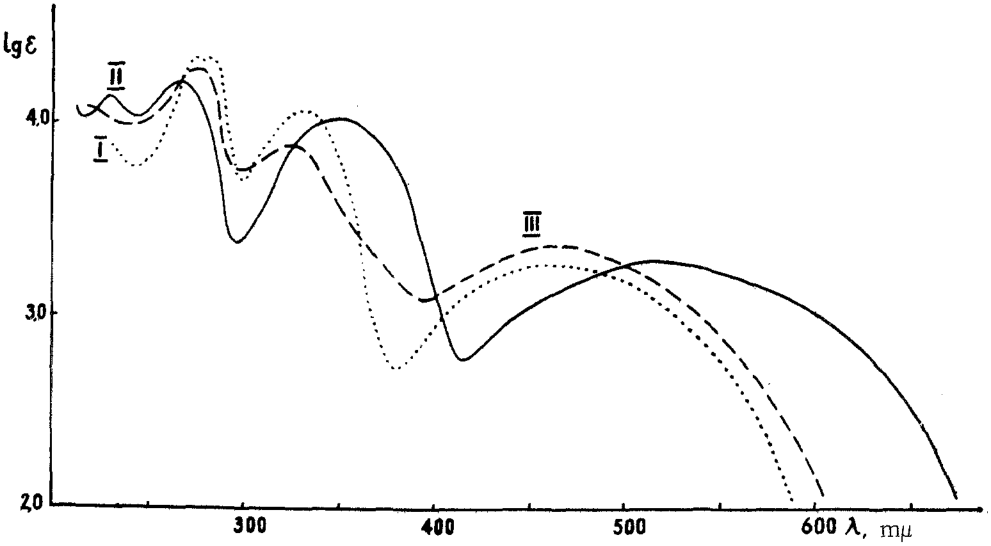
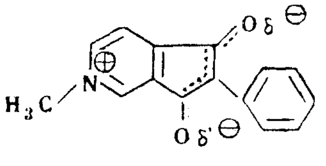
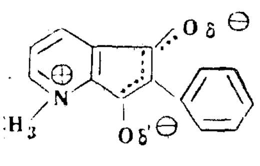


Fig. 2. UV spectra of 2 × 10^{-5} M solutions of 2-phenyl-5-azaindan-1, 3-diones in 50% ethanol containing:
I - 2 mole/l KOH (IIA); II - 0.1 mole/l H_2SO_4 (IIB); III - 2 mole/l HCl (VIa)



IV



V

Dissociation of III is usually repressed [7] in acid solutions (0.1 M HCl), and, depending on the solvent, the diketone or enol form predominates. In the actual case of 2-phenylazaindandiones in 0.1 M sulfuric solution there is no protonation at the oxygen atom, whence it follows that the enol forms of N-protonated or methylated 2-phenylazaindandiones are strong acids, and completely dissociated in acidified water-alcohol solution at ca. pH 0.7.

We investigated solutions of I and II and their N-betaines (IV and V) in 50% ethanol containing 2 mole/*l* HCl. Under these conditions II and IV have almost identical absorptions (Figs. 2 and 3). The long wavelength maximum of II is displaced hypsochromically, compared with the spectrum of II in a solution containing 0.1 mole/*l* H_2SO_4, and is situated at 470 mμ (ε 2300). The increased hydrogen ion concentration facilitates protonation of the oxygen atom, and here the hydrochloride of the N-protonated, or N-methylated, 2-phenyl-5-azaindandione, VIa and VIb, respectively, is indeed formed.

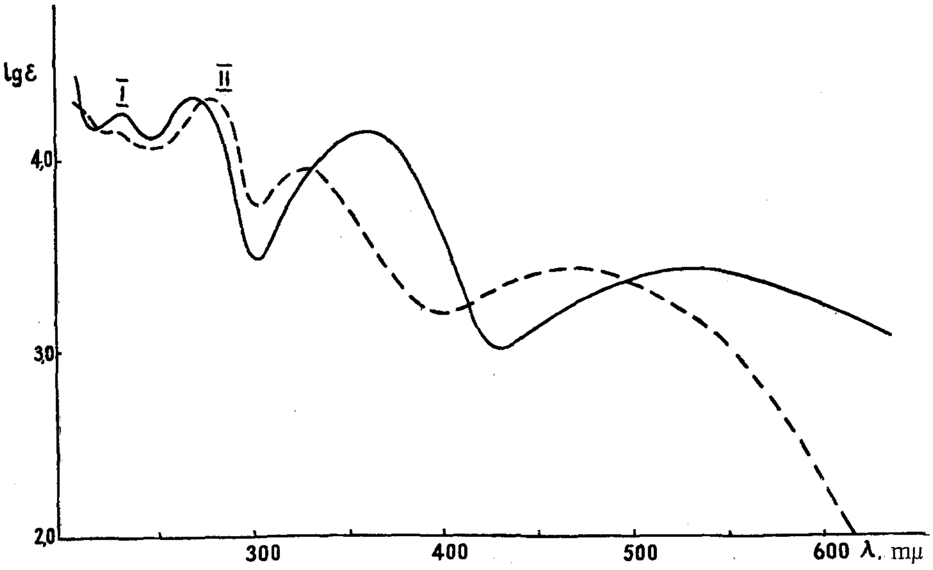


Fig. 3. UV spectra of 2-phenyl-5-azaindan-1,3-dione N-methylbetaine (IV): I — 2 × 10^{-5} M solution of IV in 50% ethanol containing 2 mole/*l* HCl; II — 2 × 10^{-5} M solution of IV in 50% ethanol

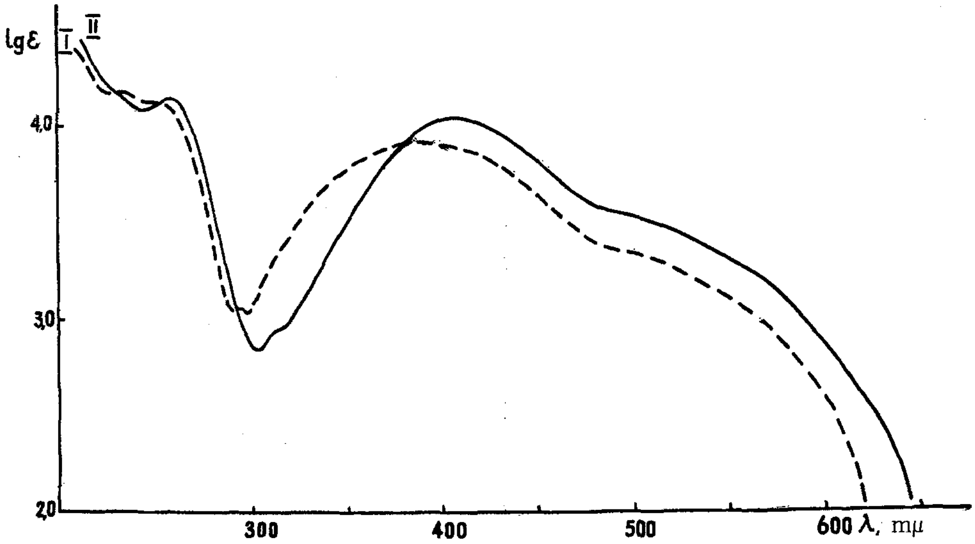
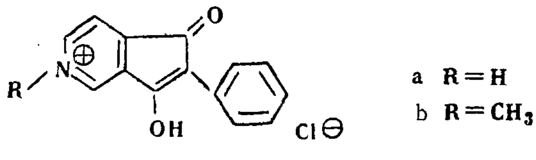


Fig. 4. UV spectra of 2-phenyl-4-azaindan-1,3-dione N-methylbetaine (V): I — 2 × 10^{-5} solution of V in 50% ethanol; II — 2 × 10^{-5} solution of V in 50% ethanol containing 2 mole/*l* HCl



VI

The spectra of I and V in 50% ethanol, containing 2 mole/*l* HCl, also have approximately the same character (Fig. 4), but clearly differ from the absorption curves of the 5-azaindandiones just considered under the same conditions. Both solutions of I and V in 2 M HCl have an absorption maximum at 392-394 mμ (ε 7300-8300), passing into a wide bathochromically-displaced branch in the range 460-570 mμ (ε 2800-1200). This spectrum picture is more reminiscent of the betaine forms (IB and V) than of the enols of β-dicarbonyl compounds, and indicates that even in 2 M HCL there is insignificant protonation of I and V at the oxygen atom to give enol forms of pyridinium compounds, which are stronger acids than the corresponding derivatives of 5-azaindandione VIa and VIb.

From these experiments it may be concluded that the deep coloration of 2-phenylazaindan-1, 3-diones is connected with the appearance of betaine forms, which are impossible for a 2-phenylindandione. The question of the assumed association, and its significance for the properties exhibited by 2-phenylazaindandiones, requires further research.

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14 October 1964

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