ELECTRONIC ABSORPTION SPECTRA AND PROTOLYSIS OF 4- AND 5-AZAINDAN-1,3-DIONES

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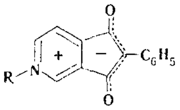
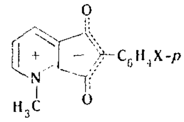
The protolytic equilibria in a series of 2-aryl-substituted 4- and 5-azaindan-1,3-diones and the corresponding N-methylbetaines and 5,6-benzo analogs were studied by spectrophotometry. The substantial difference between the 4- and 5-aza derivatives is explained by the different effect of the anionic system on the π-electron density and the reactivities of the nitrogen atoms in the 4 and 5 positions. The protonation and deprotonation constants of the dipolar ions correlate linearly with the σ° constants of the substituents in the 2-phenyl ring. In the case of 5,6-benzo-4-azaindan-1,3-diones, the keto group of the azaphthaloyl ring is protonated along with the dipolar ion in strongly acidic media.

In preceding papers [1, 2] it has been demonstrated that, depending on the pH of the medium, equilibrium between the N-protonated enol, the dipolar ion, and the anion is set up in aqueous solutions of 2-phenyl-4- and 2-phenyl-5-azaindan-1,3-diones, while equilibrium is set up between the N-methylated enol and the dipolar ion for the corresponding N-methylbetaines. The presence of the diketo form characteristic for 2-arylindan-1,3-diones in aqueous media [3] was not observed, but at the same time unusually high acidity of the N-protonated or methylated enol forms of the investigated substances (pK on the order of zero and even −1) was noted. On the basis of the previously proposed [2] scheme of the protolytic equilibria, in the present paper we have studied the change in the acidity of the 4- and 5-azaindan-1,3-diones under the influence of such factors as the electronic effects of substituents in the 2-phenyl ring, the position of the nitrogen heteroatom in the azaphthaloyl ring, annelation of the azaphthaloyl ring, etc.

The appropriate conclusions were drawn on the basis of a spectrophotometric determination of the protolysis constants of a number of previously uninvestigated 4- and 5-azaindan-1,3-diones (the formulas of the compounds are presented in the dipolar form, which is most characteristic for the solid state of the substances).


Ia, b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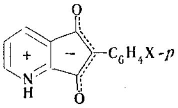
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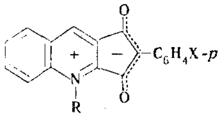
IVa, b

I a $R=H$, b $R=CH_3$; II a $X=H$, b $X=\overset{+}{N}(CH_3)_3$, c $X=N(CH_3)_2$;

III a $X=H$, b $X=OCH_3$, c $X=NO_2$, d $X=N(CH_3)_2$; IV a $R=CH_3$, $X=\overset{+}{N}(CH_3)_3$, b $R=H$, $X=N(CH_3)_2$

The numerical values of the protolysis constants of various forms of 4- and 5-azaindan-1,3-diones and the characteristics of the electronic absorption spectra (EAS) of aqueous solutions of the investigated compounds are presented in Tables 1 and 2.

It follows from a comparison of Ia and IIIa that the basicity of the nitrogen atom and the character of the EAS depend substantially on whether there is a heteroatom in the 4 or 5 position of the azaphthaloyl ring (Tables 1 and 2). The reason for the differences should be sought in the different interaction of the

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TABLE 1. Protolysis Constants of 2-Aryl-4- and -5-azaindan-1,3-diones in Aqueous (+1% C_2H_5OH) Media

Compound	$pK_{C=\overset{+}{O}H}$*	pK_{OH}†	$pK_{\overset{+}{N}H}$‡	$pK_{\overset{+}{N}H(CH_3)_2}$**
Ia	—	−0,16±0,03	5,24±0,03	—
Ib	—	0,07±0,03	—	—
IIa	—	−0,86±0,04	—	—
IIb	—	−1,38±0,02	—	—
IIc	—	−1,34±0,03	—	5,43±0,05
IIIa	—	−0,51±0,07	3,94±0,05	—
IIIb	—	−0,35±0,05	4,31±0,02	—
IIIc	—	~ −1,7	~3,1	—
IIId	—	−1,19±0,02	3,60±0,05	6,14±0,05
IVa	6,31±0,10	−1,78±0,04	—	—
IVb	~ −2,0	~1,0	3,52±0,07	6,20±0,04

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*Index of the acidity of the protonated carbonyl group in the 3 position of the azaphthaloyl ring in the N-methylated or protonated enol.

†Index of the acidity of the hydroxyl group in the 1 position of the azaphthaloyl ring of the N-methylated or protonated enol.

‡Index of the acidity of the nitrogen heteroatom in the 4 or 5 position of the azaphthaloyl ring of the dipolar ion.

**Index of the acidity of the nitrogen atom of the $-\overset{+}{N}H(CH_3)_2$ group in the p position of the 2-phenyl ring.

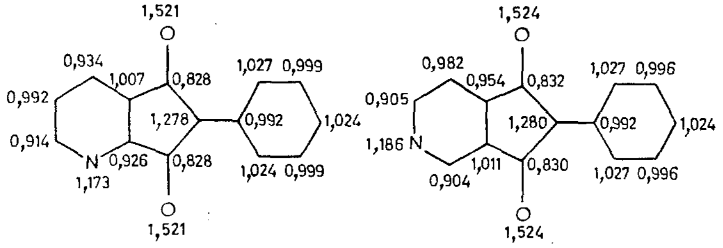

Fig. 1. Distribution of the π-electron density in the anions of 2-phenyl-4- and 2-phenyl-5-azaindan-1,3-diones.

anionic system with the atoms in the 4 or 5 positions. Calculations of the anion of 2-phenylindan-1,3-dione by the MO LCAO method [4] have shown that the 5 position is characterized by a higher π-electron density than the 4 position. This is also the case in the anions of azaindandiones. The reactivity of the unshared pair of electrons of the nitrogen atom in turn depends on the orbital electronegativity, which is a function of the state of the hybridization of the atom and the density of the π electrons on this atom: the higher the density of the π electrons, the higher the reactivity of the unshared pair of electrons. This is confirmed by preliminary calculations of the 4- and 5-azaindan-1,3-dione systems (Fig. 1). The high acidity of enol forms Ia and IIIa and of the remaining compounds is apparently due to the strong inductive effect of the positively charged nitrogen atom.

The results of the quantum-chemical calculation of the π-electron system of dipolar ions of 4- and 5-azaindan-1,3-diones do not make it possible to draw an unambiguous conclusion as to whether protonation of the carbonyl group in the 1 or 3 position is involved. It seems likely that the oxygen atom in the 1 position is protonated, as attested to by the results of a study of the annelated analogs presented below.

The dependence of the protolysis constants on the electronic effect of substituents X was investigated for a number of 2-aryl-4-azaindan-1,3-diones. Linear correlations between the corresponding acidity indexes and the σ° constants of substituents X in the p position of the 2-phenyl ring were obtained for both the protonated enol forms and the dipolar forms:

$$pK_{OH} = -0.52 - 1.17\sigma^\circ;\quad r = 0.99, \tag{1}$$

$$pK_{\overset{+}{N}H} = 4.08 - 0.62\sigma^\circ;\quad r = 0.93. \tag{2}$$

In view of the considerable distance of the reaction center from substituent X in the case of protolysis of the dipolar forms, the corresponding ρ° constant is low.

TABLE 2. Electronic Absorption Spectra of Various Forms of I-IV

Compound	N-methylated or protonated enol with a protonated C=O group	N-methylated or protonated enol	Dipolar ion	Anion
Ia	—	282 (22000), 315 (6800), 460 (2500)	232 (15600), 275 (16800), 345 (11800), 525 (2200)	223 (20000), 280 (26400), 326 (9100), 470 (2000)
Ib	—	282 (20800), 325 (6800), 465 (2700)	235 (16700), 273 (17600), 352 (11900), 530 (2000)	—
IIa	—	240 (14100), 345 (10900)	255 (12800), 397 (11400), 500 (3300)*	—
IIb	—	252 (16600), 338 (12400), 470 (1200)	267 (12200), 390 (13400), 510 (2600)*	—
IIc	—	252 (16000), 340 (11600)	† 267 (12200), 390 (13900), 495 (3400)* ‡ 264 (17800), 424 (14200), 540 (3600)*	—
IIIa	—	240 (12000),* 345 (11600), 450 (1900)*	255 (12800), 393 (12100), 500 (2700)	260 (15100), 340 (14900), 460 (2100)
IIIb	—	235 (15800), 358 (11500), 460 (2400)*	255 (15300), 402 (13400), 510 (2300)*	260 (17400), 345 (15100), 462 (2000)
IIIc	—	290 (2500),* 355 (8100)	255 (5500),* 420 (8800)	260 (7100),* 305 (2500),* 420 (10000)
IIId	—	251 (16400), 339 (13800), 415 (3400)*	264 (12900), 388 (15400), 495 (3400)*	† 270 (13000),* 342 (18000), 415 (3800),* 465 (2600)*
IVa	243 (12500),* 290 (21700),* 314 (34000), 375 (8750)*	280 (2500), 313 (24800), 370 (13200)*	275 (39600), 320 (8200), 408 (14600), 475 (9200)*	‡ 270 (18000), 352 (20000), 465 (2000)
IVb	238 (17000),* 270 (20500),* 312 (41500), 382 (14000)	Not obtained because of the low solubility of the form	274 (26800), 320 (8600), 410 (15200), 480 (10000)*	† 255 (31400), 318 (31600), 385 (17000) ‡ 258 (29600), 325 (23400), 400 (18000)

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* Inflection.

† With a protonated $-N(CH_3)_2$ group.

‡ With a deprotonated $-N(CH_3)_2$ group.

The $\rho°$ constants for the enol forms of 2-aryl-4-azaindan-1,3-diones are closer to the $\rho°$ value (1.28) found for the enol forms of 2-arylindan-1,3-diones in 50% aqueous ethanol and differ considerably from the value for the diketo form of the indicated compounds ($\rho° = 2.23$) [5]. This fact is an additional confirmation of the enol structure of 2-aryl-4- and -5-azaindan-1,3-diones in acidic media, which was previously predicted on the basis of an analysis of the EAS [2].

The pK_{OH} and $pK_{\overset{+}{N}H}$ values for 2-(p-nitrophenyl)-4-azaindan-1,3-dione do not follow correlation equations (1) and (2). The p-nitro group apparently affects the acid–base properties not only by means of the polar effect but also by direct conjugation with the reaction center. Also speaking in favor of a different (from other compounds of this series) structure is the peculiarity of the EAS of IIIc (Table 2), which undergo only insignificant changes during prototropic transformations, while the EAS of the different forms for the remaining investigated compounds differ considerably from one another.

The MO calculations for 2-(p-nitrophenyl)indan-1,3-dione showed that the character of the EAS and other physicochemical characteristics of this compound are determined primarily by the contribution of the nitro group rather than by that of the indan-1,3-dione grouping to the π-electron structure of the conjugated system.

The effect observed during annelation of the azaphthaloyl ring is unexpected. The EAS of solutions of IVa in sulfuric acid (8-14 M) form a set of curves with well-expressed isosbestic points; this is evidence for further protonation of N-methylbetaine, because the formation of a methylated enol proceeds at sulfuric acid concentrations up to 7 M. The absorption of IVa in concentrated sulfuric acid should evidently be ascribed to the cation that is formed as a result of the protonation of the oxygen atom of the carbonyl group ($pK_{C=\overset{+}{O}H}=-6.31$) and altogether bears three positive charges.

The direct observation of this sort of process in the case of IVb is hampered, first, by the closeness of the $pK_{C=\overset{+}{O}H}$ and pK_{OH} values and, second, by the anomalously low solubility of the enol form. One may suppose that the reason for the decreased solubility of the enol form is the formation of an intramolecular hydrogen bond between $\overset{+}{N}H$ and $C=O$, which is destroyed when the acidity of the medium is increased, i.e., because of protonation of the carbonyl group. The similar character of the EAS of IVa and IVb in concentrated sulfuric acid solution is evidence in favor of the occurrence of precisely this process, which brings about dissolving of the substance. It must be assumed that the stabilization of the structures with three positive charges occurs through expansion of the conjugated π-electron system when a benzene ring is introduced into the 5,6 position, for this sort of process cannot be observed in the case of IIb, IIc, and IIId, or other 4-azaindan-1,3-diones.

However, the protonation of the carbonyl group in strongly acidic media to give a cation of mesomeric structure cannot be assumed to be specific for annelated 4-azaindan-1,3-diones. We have also observed similar phenomena in strongly acidic solutions of 2-arylindan-1,3-diones [6].

EXPERIMENTAL

Aqueous solutions ($6 \cdot 10^{-5}$-$2 \cdot 10^{-6}$ M) of I-IV containing 1% ethanol were investigated at various pH values by a spectrophotometric method with SF-4 spectrophotometers and a UV-2 recorder. Sulfuric (0.1-17 M) and hydrochloric (0.01-1 M) acids and acetate (pH 3.5-5.6) and phosphate (pH 5.9-6.9) buffer solutions, and potassium hydroxide solution (pH 12) were used to create media with a definite acidity. The pH of solutions of I-IV containing buffer mixtures (10^{-3} M with respect to one of the components) were measured with an LPU-01 device calibrated with respect to biphthalate and borate buffer solutions. The accuracy of the determinations was ± 0.02 pH unit. The concentrations of the sulfuric acid solutions were determined by alkalimetry, and their acidities were characterized by the Hammett acidity function (H_0) [7]. The pK values were calculated from the formula

$$pK = pH(H_0) + \lg\frac{[HA]}{[A]}$$

without correction for the ionic strength of the solutions, in view of the low concentration of the buffer mixtures. The investigations were carried out at 20 ± 1°.

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