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Dyes and Pigments 53 (2002) 219–227

DYES and PIGMENTS

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Deprotonation and protonation studies of some substituted 1,4- and 9,10-anthraquinones

Tzvetanka Philipova[a,*], Christina Ivanova[a], Yavor Kamdzhilov[a], María Teresa Molina[b]

[a]*University of Chemical Technology and Metallurgy, 8 Kl.Ohridski Blvd., 1756 Sofia, Bulgaria*
[b]*Instituto de Química Médica (CSIC), Calle Juan de la Cierva 3, 28006 Madrid, Spain*

Received 5 December 2001; received in revised form 29 January 2002; accepted 8 February 2002

Abstract

Ground and excited state deprotonation and protonation pK_a values of anthraquinones with amino, hydroxy and chloro substituents were determined by means of spectrophotometric titrations and Förster cycle calculations. In the mixed amino-hydroxy 9,10-anthraquinones a second stage of deprotonation and protonation was not registered, and only when the primary amino function is attached to an electron-withdrawing group (–$COCH_2Cl$) a second ionization takes place. Acidity of the hydroxy-1,4-anthraquinones in the ground state is about 2.5 pK_{a-} units higher than that of the related 9,10-anthraquinones. The determined values of pK_{a+} of protonation are within the limits of −4.46 up to −8.39. The calculated values of the excited state of deprotonation are in the range 1.15–2.57, while the excited state values for protonation vary from 0.91 to 2.57 correspondingly. It was concluded that a proton transfer in the excited state is possible for all the investigated compounds. © 2002 Published by Elsevier Science Ltd.

Keywords: Anthraquinones; Deprotonation; Protonation; Excited state intramolecular proton transfer (ESIPT); pK; Acidity; Basicity

1. Introduction

Anthraquinones are extremely important taking into account their properties and broad field of their application [1]. So, hydrogen atom transfer and electron transfer reactions are of great importance as primary processes in both chemistry and biochemistry [2], and in these processes anthraquinones play an important role because they act as H-atom and electron acceptors in the excited state [3–6]. Anthraquinone-containing electrofunctional polymers acting as electron transfer mediators have been used in the development of biosensors [7].

The anthraquinone chromophoric system has been used extensively for many years for the preparation of textile dyes [8–10]. The hue of anthraquinone dyes is essentially controlled by the presence of electron donors, such as amino and hydroxyl groups in the 1-, 4-, 5-, and 8-positions of the nucleus. Their colorant properties related with the absorption maxima of quinones have been studies by Pariser–Parr–Pople molecular orbital (PPP MO) methods [11]. Aminoanthraquinones are the basic structures of the disperse dyes, which are one of the most important

* Corresponding author.

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PII: S0143-7208(02)00016-5

family of dyes, characterized by good fastness properties and brightness. They provide bright red to blue shades. In addition, anthraquinone vat dyes (leuco dyes) is the largest and most important class of vat dyes [12]. In this group are included the acylamino anthraquinones which possess mainly yellow and orange dyes. In addition, anthraquinones have become recently very important in the high technology industries of electronic and particularly reprographics. Thus, some aminoanthraquinone derivatives are used in transfer printing toners and others are used in thermal printing [13–16]. Moreover, other colorants such as quinone cyanine dyes are the subject of recent studies [17].

The possibility of excited state proton transfer, which has attracted much attention in recent years, can be derived immediately by comparison of ground and excited state protonation and deprotonation parameters. The pK_a values provide important data about the chemical properties of anthraquinones. In most cases the reactions of hydroxy and amino derivatives of 9,10- and 1,4-anthraquinones occur in acidic or alkaline medium [1]. For better understanding and controlling these reactions, it is important to know in what state are present the derivatives of anthraquinone in the reaction medium. There are no reports in the literature concerning pK_a interactions of 1-amino-4-hydroxy-9,10-anthraquinone and its acyl derivatives as well as of hydroxy-1,4-anthraquinones in alkaline and acidic medium. However, the acidity constants of several 1-hydroxy-9,10-anthraquinone derivatives in various methanol-water mixtures have been determined by spectrophotometric methods [18]. After our work was finished, the pK_a values of a number of naturally occurring hydroxy-9,10-anthraquinones, determined by capillary electrophoresis, have been published [19].

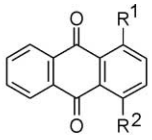
In this paper, we report on the structure of both protonated and deprotonated forms of substituted amino- and hydroxy-anthraquinones and the possibility of excited state proton transfer by means of spectrophotometric titration and Förster cycle calculation.

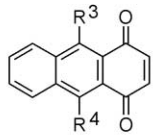
Substituted anthraquinones with the structure shown in Scheme 1 have been studied.

2. Results and discussion

2.1. Deprotonation

The results for the deprotonation experiments of compounds **1**–**5** are shown in Table 1. Deprotonation of the investigated compounds **1**–**5** leads to a bathochromic shift of the absorption bands in the visible region, because the phenoxide moiety possesses a much stronger electron donor ability than the OH group ($\Delta\lambda = 86$–136 nm). Fig. 1 displays the influence of pH on the visible absorption spectra of some of these compounds. The pK_a values in the ground state of **1**–**3** (Table 1) are comparable with those of 1,4- and 1,5-dihydroxy-9,10-anthraquinones (pK_{a-} are 9.9 and 9.6; and pK_{a--} are 11.2 and 11.1 respectively) [20]. In the





Compound	R^1	R^2	R^3	R^4
1	NH_2	OH	-	-
2	$NHCOCH_2Cl$	OH	-	-
3	$NHCOC(CH_3)=CH_2$	$OCOC(CH_3)=CH_2$	-	-
4	-	-	OH	H
5	-	-	OH	Cl

Scheme 1.

1,4-dihydroxy-9,10-anthraquinone (quinizarine) spectrum at higher pH values, two maxima of the long wave absorption band are seen, which are indicative of the dibasic anion. In the case of compounds **1** and **2**, the spectra show two absorption maxima in the range of 530 to 600 nm upon increasing the pH of the solutions, but an interesting peculiarity was observed for compound **1**. Under the experimental conditions, only one value for pK_{a-} (10.80) was determined within the range of the two maxima, most likely the proton released coming from the amino group. Thus, the obtained monobasic anion **1a**$_-$ is stabilized via an additional intramolecular hydrogen bond resulting in two 6-member chelate rings. As a consequence of this, an electron symmetry for the whole molecule arises, which leads to stabilization of the two carbonyl groups. Over the investigated pH interval, a second stage of deprotonation was not registered. Although amines are basic compounds, the basicity of the aminoanthraquinones is extremely low due to the strong polarizing effect of the quinone C=O group on the aminogroup [21]. The tendency to formation of a second step corresponding to the

Table 1
Deprotonation of compounds **1–5** in the ground and excited states

Compound	λ (nm)	λ_- (nm)	$\varepsilon_\lambda/\varepsilon_{\lambda-}$	λ_{--} (nm)	$\varepsilon_{\lambda-}/\varepsilon_{\lambda--}$	pK_{a-}	pK_{a--}	pK^*_{a-}	pK^*_{a--}
1	460	534 570	0.188	–	–	10.80±0.06		2.00	–
2	466	560 600	0.745	560 600	0.633	10.11±0.02	13.01±0.13	2.56	2.57
3	414	550	0.859	–	–	10.25±0.04	–	2.28	–
4	474	570	0.980	–	–	8.78±0.01	–	1.15	–
5	468	554	1.010	–	–	8.64±0.06	–	1.59	–

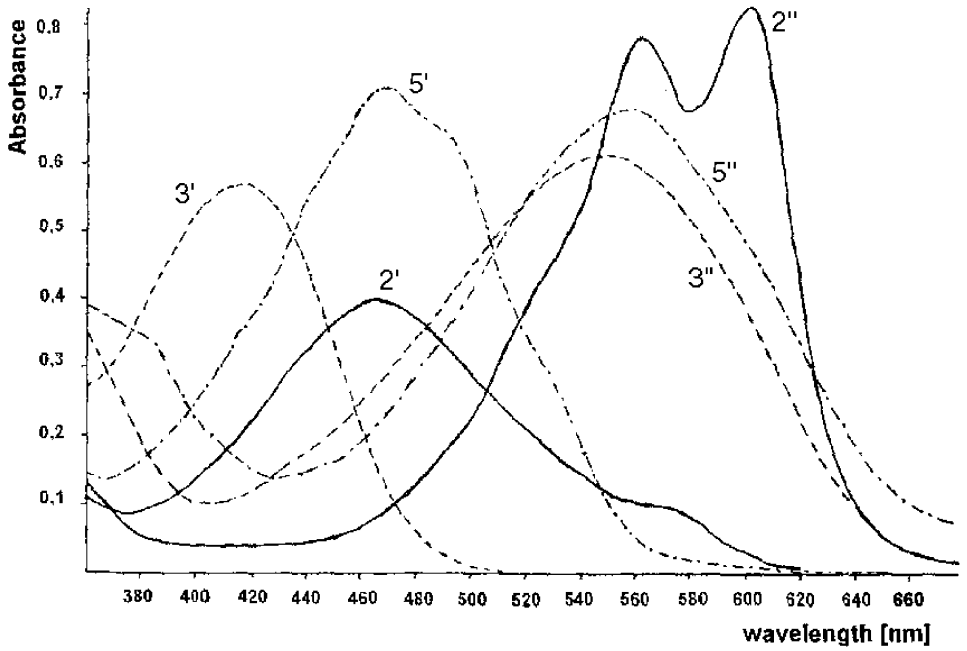


Fig. 1. Absorption spectra of nondeprotonated and deprotonated forms of compounds **2** (—), **3** (- - - -) and **5** (–·–·–). pH: **2**′, 7.48; **2**″, 13.60; **3**′, 6.10; **3**″, 12.60; **5**′, 5.38; **5**″, 11.30.

deprotonation of the hydroxy group was not observed for the compound **1**. This takes place at higher values of pH (13.5–14) and the experimental determination of the second constant is impossible. On the other hand, for compound **2**, containing both secondary amino and hydroxy groups, two pK_a values were measured (see Fig. 2). Thus, the monobasic anion of the deprotonated **2a**$^-$ is present in the interval of pH 9.4 to 10.8 (pK_{a-} = 10.11) while in the interval of pH 13–13.5 prevails the dibasic anion **2a**$^{--}$ (pK_{a--} = 13.01). This can be explained by the strong electron-withdrawing effect of the chloroacetyl group, which stabilizes the adjacent negative charge on the nitrogen atom (**2a**$^-$**)** by delocalization with the carbonyl group of the substituent. This enables a second stage of deprotonation (**2a**$^{--}$**)**, the pK_{a--} being two order of magnitude higher than the corresponding to dihydroxy substituted anthraquinones.In the case of compound **3**, containing only a secondary amino group, it displays an increased acidity (pK_{a-} = 10.25) compared to that of compound **1**. The existence of electronic conjugation between the carbonyl group and the double bond of the substituents R^1 and R^2 (**3**) weakens the strength of the hydrogen bond and facilitates its deprotonation. The obtained protolytic constant of **3**, which does not contain OH group, corresponds well to the pK_a-values of the compound **1** and this result is a good confirmation of the supposed mechanism of deprotonation of **1**.

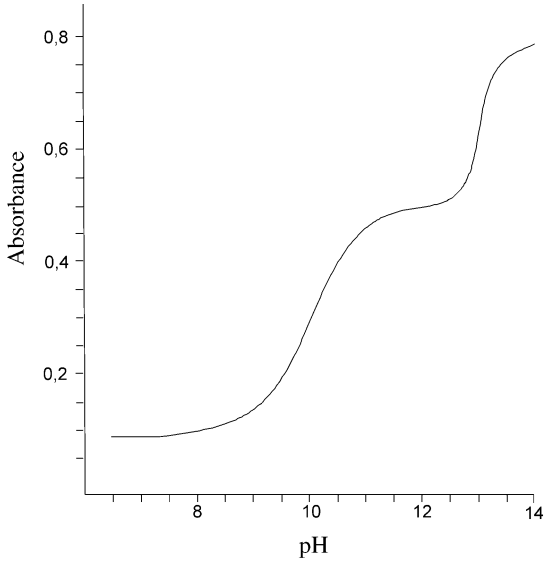
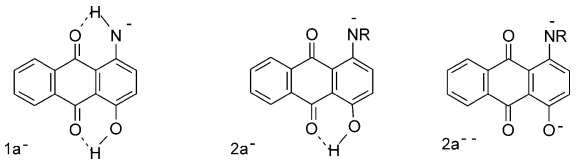


Fig. 2. The effect of pH on the absorption of compound **2** at 560 nm.



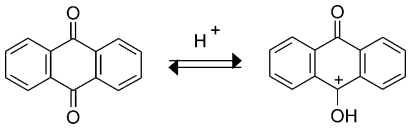
All three compounds **1**–**3** possess a labile hydrogen atom (NH) and the electron-donating groups (amino and/or hydroxy) are conjugated with the quinone carbonyl group forming a hydrogen bond. The data, presented in Table 1, shows that the presence of a free hydroxy group in **2** leads to lowering acidity in comparison with **3** where the hydroxy group is acylated.

In contrast to 9,10-anthraquinones, in the literature there are no data for the pK_a values of hydroxy-1,4-anthraquinones. It is well known that the hydroxy group in 1-hydroxy-9,10-anthraquinone can be deprotonated with more difficulty compared to that in the 2-hydroxy derivative due to the intramolecular hydrogen bond formation [20]. This is reflected on the measured values of pK_a which are 11.5 and 7.6, respectively. From the data in Table 1, acidity of **4** in the ground state is about 2.7 pK_a units higher than of the corresponding 1-hydroxy-9,10-anthraquinone [22]. These results evidence that the O–H bond in 9-hydroxy-1,4-anthraquinone is less stable than the bond in 1-hydroxy-9,10-anthraquinone, so that reactions such as alkylation, acylation and tosylation run under milder conditions. The presence of a Cl atom in opposite position respect to the hydroxy group enhances the acidity. The negative inductive effect of the Cl atom is greater in absolute value than the positive mesomeric effect, thus playing a dominant role in facilitating deprotonation.

2.2. Protonation

As many reactions for the preparation of anthraquinone dyestuffs are carried out in highly concentrated sulfuric acid as a solvent, it is useful to know that under such conditions anthraquinone is protonated at one of the carbonyl oxygens

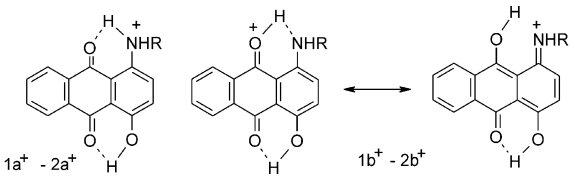
($pK_a = -8.40$, $\lambda = 413$ nm), as determined by Kratochvíl and Nepraš in a series of amino and chloro anthraquinones [23].



Later, Gorelik [24] examined the acidic properties of a number of hydroxy anthraquinones using the same spectrophotometric method.

The introduction of a hydroxy group at position 1 on going from 9,10-anthraquinone to 1-hydroxy-9,10-anthraquinone leads to increased basicity by $\Delta pK_a = 1.4$ [24]. 9,10-Anthraquinones, containing primary or secondary amino groups at position 1, are much more sensitive to the action of acids compared to the 2-isomers, because the substituents at position 1, if possible, can form an intramolecular hydrogen bond which lowers their basicity. It is a well known fact, that the transition from primary to secondary and tertiary amino group is associated with a substantial increase in basicity [25].

We wish to report herein on the behavior of 9,10-anthraquinone derivatives containing both amino and hydroxy groups. The results for the protonation of compounds **1–5** are listed in Table 2. The determination of the protolytic constants (pK_{a+} and pK_{a++}) of very weak bases attaching protons in high sulphuric acid concentrations is possible only by spectrophotometry using the Hammett function (H_0). The protonation of **1–3** is accompanied by a bathochromic shift of the visible absorption band ($\Delta\lambda = 46$–62 nm). Theoretically, in **1** and **2** the proton can reside either at the nitrogen atom forming the cation $\mathbf{1a}^+$–$\mathbf{2a}^+$ or at the oxygen atom of the quinone carbonyl group with the formation of a cation $\mathbf{1b}^+$–$\mathbf{2b}^+$ stabilized by resonance. Previous studies from Kratochvíl and Nepraš [23] established that monoprotonation of 1-aminoanthraquinone takes place at the nitrogen.



In our case, under the experimental conditions, the probability of the monoprotonation to occur at the oxygen atom of the quinone carbonyl group, but not at the *N*-atom, is much greater as the obtained cations $\mathbf{1b}^+$–$\mathbf{2b}^+$ are stabilized by resonance (*ana*-quinoid forms are possible). In Fig. 3 are presented the visible absorption spectra of some of the investigated compounds on varying acidity of the solutions. Compound **1** shows only one stage of protonation ($pK_{a+} = -8.07$), occurring at the oxygen atom *peri* to the NH_2 group. The replacement of a primary amino group with a secondary one in **2** causes an increase of the pK_{a+} value by two orders of magnitude. Only in this case, the oxygen of the quinone carbonyl group in *peri*-position to the hydroxy group can be protonated in more acidic solutions. The pK_{a++} of the diprotonated form was found to be -8.39. The presence of an electron withdrawing group (C=O) in close proximity to the amino group in the substituent, $R = -COCH_2Cl$, (**2**) weakens the hydrogen bond in the cation $\mathbf{2a}^+$ thus facilitating the protonation at the oxygen of the quinone C=O group. However, in compound **1** with *R*=*H* the cation $\mathbf{1a}^+$ is stabilized by resonance and additionally the two hydrogen bonds ensure an electron symmetry for the whole molecule, thus stabilizing the two carbonyl groups, so that diprotonation does not occur.

Table 2
Protonation of compounds **1–5** in the ground and excited states

Compound	λ (nm)	λ_+ (nm)	$\varepsilon_\lambda/\varepsilon_{\lambda+}$	λ_{++} (nm)	$\varepsilon_{\lambda+}/\varepsilon_{\lambda++}$	pK_{a+}	pK_{a++}	pK^*_{a+}	pK^*_{a++}
1	398	444	0.287	–	–	-8.07 ± 0.01	–	-2.70	–
2	398	460	1.578	460	0.326	-6.08 ± 0.01	-8.39 ± 0.03	0.91	-1.40
3	430	470	0.566	–	–	-7.48 ± 0.02	–	-3.40	–
4	474	528		597	–	-4.46 ± 0.01	-8.23 ± 0.11	-2.27	-1.47
5	480	520	1.376	552	0.470	-5.77 ± 0.02	-8.35 ± 0.01	-2.46	-2.75

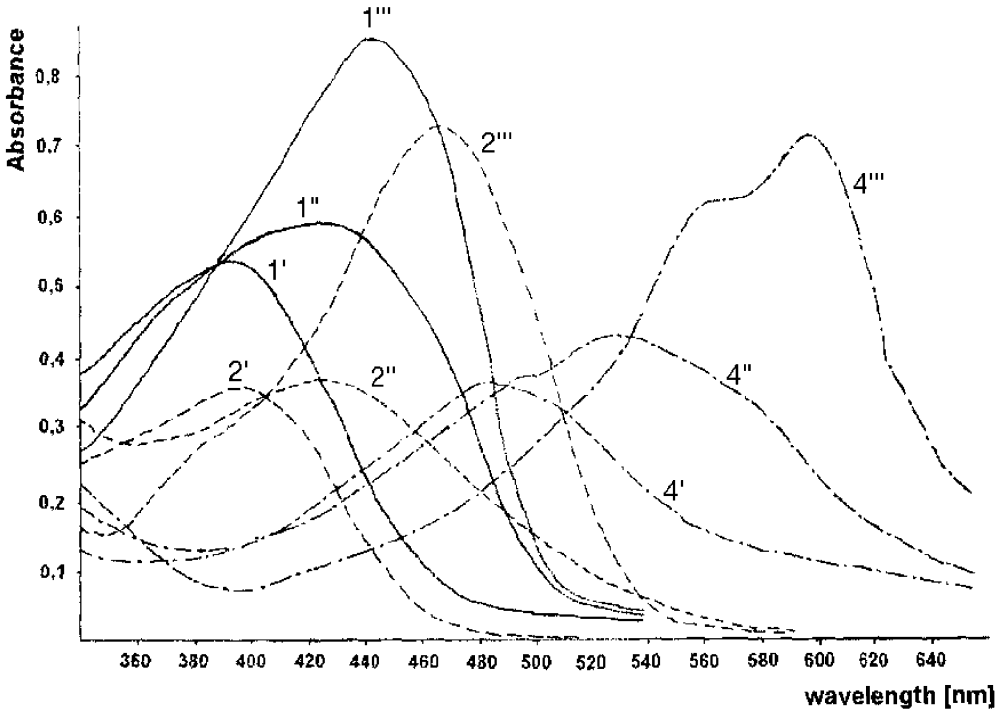


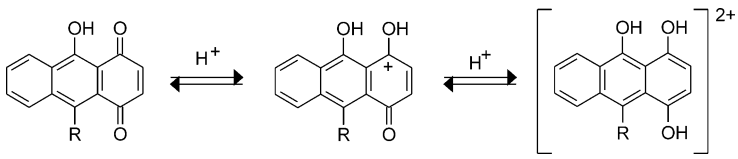
Fig. 3. Absorption spectra of nonprotonated and protonated forms of compounds **1** (—), **2** (- - - -) and **4** (–·–). H_2SO_4,% (H_0): **1**′: 70 (−5.80); **1**″: 83 (−7.81); **1**‴: 87 (−8.45) **2**′: 60 (−4.46); **2**″: 82 (−7.66); **2**′: 96 (−10.03) **4**′: 60 (−4.46); **4**″: 70 (−5.80); **4**‴: 84 (−7.97).

The protonation of compounds **4** and **5** is also accompanied by a bathochromic shift of the absorption bands ($\Delta\lambda = 40$–123 nm). This is an evidence for a proton bound to the carbonyl group conjugated to the hydroxy group. We observed that with the increase of acidity, the long-wave absorption band was shifted bathochromically with further 123 nm for **4** and 72 nm for **5**, and at more than 82 and 76% H_2SO_4 concentration respectively, no shift was detected. Therefore, the diprotonation of 9-hydroxy-1,4-anthraquinones is directed to the second carbonyl group with the formation of a dication but not to the oxygen atom of the substituent.

Therefore, in the 9-hydroxy-1,4-anthraquinones only the carbonyl groups are protonated. The hydroxy group cannot be protonated probably because of its closeness to the carbonyl group. The achieved effective conjugation makes unfavorable the formation of two neighbouring cation centers.

2.3. Excited state intramolecular proton transfer

The calculated values of excited state deprotonation and protonation of the studied substances are listed in Tables 1 and 2. The excited state pK^*_{a-} values for deprotonation of



the compounds **1**–**5** are in the region 1.15–2.57 while the excited state pK^*_{a+} values for protonation are within the interval of 0.91 up to −3.40. The highest probability for a proton transfer can be expected from compound **2,** where the pK_a gap between deprotonation and protonation in the excited state is the lowest. The data in Table 1 and 2 as well as in Fig. 4 show that the largest gap between pK^*_{a-} and pK^*_{a+} is about 5 units (compound **3**). This gives us ground to suppose that a proton transfer in the excited state is possible for all the investigated compounds.

In summary, we have determined for the first time the pK values for some 1,4-anthraquinones and have established the noteworthy differences with the corresponding 9,10-anthraquinones. We hope that these results will shed some light into a variety of biological problems and will spur further industrial applications.

At present, we are studying the quenching efficiency of some of these molecules using purple membranes as a model system [26].

3. Experimental

3.1. Materials

1 - Amino - 4 - hydroxy - 9,10 - anthraquinone (**1**) (Aldrich, USA) was purified by repeated crystallizations from cyclohexane. 1-Chloroacetylamino-4-hydroxy-9,10-anthraquinone (**2**) was synthesized by acylation of **1** with chloroacetyl chloride [27]. The preparation of 1-methacryloylamino-4-methacryloyloxy-9,10-anthraquinone (**3**) will be published elsewhere in detail [28]. 9-Hydroxy-1,4-anthraquinone (**4**) was obtained by a method described in a previous paper [29]. 10-Chloro-9-hydroxy-1,4-anthraquinone (**5**) was synthesized by the chlorination of **4** with freshly distilled $SOCl_2$ [30].

All compounds obtained were purified by flash chromatography [31] and recrystallization.

3.2. Methods

The electronic absorption spectra were measured using a Perkin-Elmer 323 spectrophotometer at 2

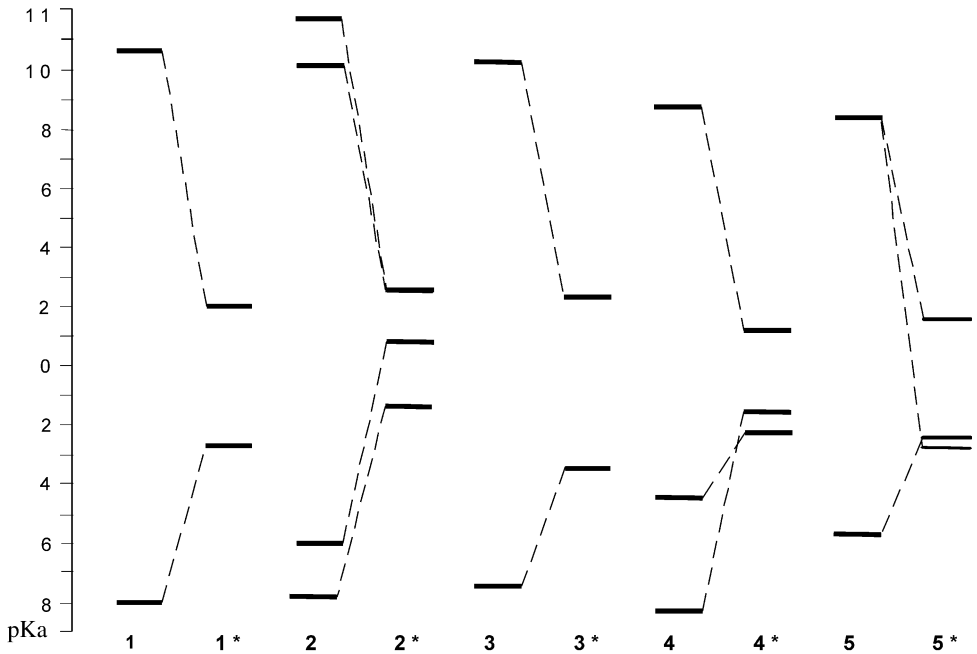


Fig. 4. Ground and excited state pK_a values for deprotonation and protonation of compounds **1–5**.

nm resolution. The absorption of the thermostated solutions was measured in 1 cm cells. All solvents were of spectroscopic grade (Merck) and were used without further purification. pH was controlled by a pH meter equipped with a glass electrode.

The pK_a values of the investigated compounds **1**–**5** were determined by spectrophotometric titrations. The deprotonation of the substances was studied by using solvent mixtures containing 40% ethanol in water. pH values lower than 10 were maintained using NH_3/NH_4NO_3 buffers with ionic strength of 0.1 while those higher than 10 with KOH solutions. The concentration of the compounds **1**–**5** was 1×10^{-4} mol l^{-1}. The protolytic constants were calculated according to Eq. (1).

$$pK_a = pH + \lg\frac{A_{max} - A}{A - A_{min}} \quad (1)$$

where A_{max} is the absorption of the deprotonated form (B^-, B^{--}), A_{min} is the absorption of a neutral molecule or monodeprotonated form and A is the measured absorption at a given pH.

The protonation was studied in sulfuric acid. The starting solutions of the investigated compounds at concentration 2.5×10^{-3} M were prepared by dissolving the corresponding samples in conc. H_2SO_4 (with exactly determined concentration). The series of solutions (1×10^{-4} or 5×10^{-5}) of the studied compounds in aqueous H_2SO_4 at different concentrations were prepared in calibrated flasks of 25 cm^3, by adding the portion of the stock solution and the calculated amount of water to make up to the mark with conc. H_2SO_4. The protolytic constants of the compounds (pK_a of the protonated carbonyl quinone groups) were calculated using the Eq. (2).

$$pK_a = H_0 + \lg\frac{A - A_{min}}{A_{max} - A} \quad (2)$$

where H_0 is the Hammett function in sulfuric acid solution [32]; A_{max} is the absorption of the fully protonated form (BH^+ or $BH_2^{+\,+}$) from the corresponding step of the curve $A = f(H_0)$; A_{min} is the absorption of the nonprotonated form; A is the measured absorption at a given value of H_0 within the investigated interval.

Due to the weak basicity of the compounds, in some cases the values of A_{max} and A_{min} were not correctly defined (do not correspond to strictly horizontal portion of the curves $A = f(H_0)$). To avoid this, a transformed variant of Eq. (1) and a graphical method of finding their values was used. The equations of the corresponding straight lines are:

$$A = A_{min} + \frac{1}{K_a}\cdot h(A_{max} - A);$$
$$A = A_{max} - K_a\left(\frac{A - A_{min}}{h}\right) \quad (3)$$

where: $H_0 = -\lg h$

For all the studied compounds the absolute value of the slope of the linear relationship [Eq. (4)].

$$\mathrm{Ig}\frac{A_{max} - A}{A - A_{min}} = f(H_0) \quad (4)$$

is equal to $1.00 + 0.05$.

Acknowledgements

M.T.M. and T.P. acknowledge the Spanish–Bulgarian Commission for the Joint Project 98 BG0013 and a visiting fellowship to Dr. Tz. Philipova.

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