

## Influence of substituent on spectroscopic and acid-base properties of anthraquinone derivatives

(INDEX: 50-55/2010 Copernican Letters® Vol 1)

Anna Bigo<sub>ł</sub>, Paweł Niedziałkowski, Justyna Czupryniak, Dorota Zarzeczkańska,  
Tadeusz Ossowski

University of Gdańsk, Faculty of Chemistry, Department of Analytical Chemistry,  
ul. Sobieskiego 18/19 80 – 952 Gdańsk  
E-mail: anna.bigot@chem.univ.gda.pl

### Abstract

A series of 1,4-disubstituted aminoanthraquinones has been prepared from 1,4-ditosyloksyanthraquinone. The potentiometric and UV-spectrophotometric method have been used to study the acid-base properties of obtained compounds. The absorption spectra revealed the presence of vibronic band in visible region for compounds containing two tertiary nitrogen groups. It indicates the separation of vibronic states in the molecule. Determined  $pK_a$  values in acetonitrile used as a solvent indicate the influence of substitution of amino group on basicity of the anthraquinone moiety.

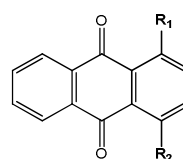
### 1. Introduction

Anthraquinone and its derivatives are important compounds used in the field of dyes and pigments [1,2]. The anthraquinones are also commonly used in medicine, especially the aminoalkylamino-disubstituted in position 1,4 express anticancer and antitumor activity.

The spectroscopic properties of anthraquinones are well documented. The position of the substituent affects not only spectroscopic properties of the compound by charge transfer interaction with the ring system, but also changes its acid-base and complexometric properties [3]. The anthraquinone chromophoric system has been used extensively for many years for the preparation of textile dyes. The hue of anthraquinone dyes can be controlled by the presence of electron donors groups in anthraquinone ring. The most often are used amino and hydroxyl groups substituted in the 1-, 4-, 5- and 8- positions [4].

Anthraquinones are extremely important taking into account their properties and broad field of their application. Hydrogen atom transfer and electron reactions are of great importance as primary processes in both chemistry and biochemistry, and in these processes anthraquinones play an important role because they act as H-atom and electron acceptors in the excited state. Anthraquinones containing electrofunctional polymers acting as electron transfer mediators have been used in the development of biosensors. They are often used in chemical sensors as a spectroscopic indicators of complex formation process [4].

The structures of investigated anthraquinone derivatives are shown in Figure 1.

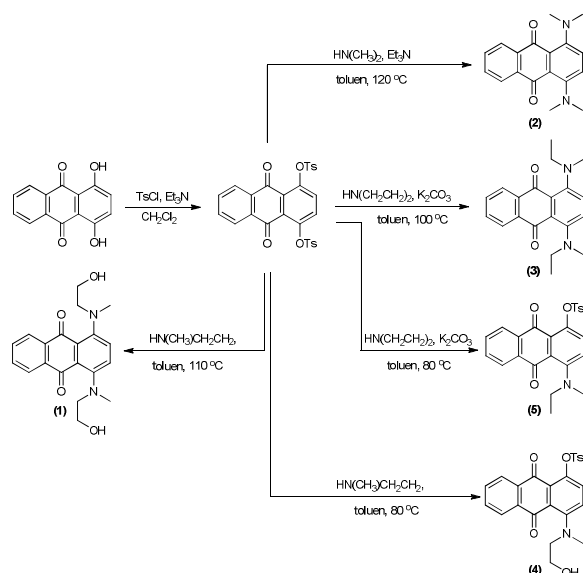


- |     |                            |                            |
|-----|----------------------------|----------------------------|
| (1) | $R_1 = -N(CH_3)CH_2CH_2OH$ | $R_2 = -N(CH_3)CH_2CH_2OH$ |
| (2) | $R_1 = -N(CH_3)_2$         | $R_2 = -N(CH_3)_2$         |
| (3) | $R_1 = -N(CH_2CH_3)_2$     | $R_2 = -N(CH_2CH_3)_2$     |
| (4) | $R_1 = -O-Tos$             | $R_2 = -N(CH_3)CH_2CH_2OH$ |
| (5) | $R_1 = -O-Tos$             | $R_2 = -N(CH_2CH_3)_2$     |

Fig. 1. The chemical structures of investigated 1,4-anthraquinone derivatives

## 2. Experimental Synthesis

The series of new 1,4-anthraquinone derivatives was prepared by the reaction of displacement of 1,4-ditosyloksy-anthraquinone shown on Scheme 1.



**Scheme 1.** Synthesis of 1,4-anthraquinone derivatives.

All compounds were synthesized from 1,4-di-*p*-toluenosufonyloksy-9,10-anthraquinone, obtained previously from 1,4-dihydroksy-9,10-anthraquinone [5,6]. The compounds (1), (2), (3) were prepared by the reaction of 1,4-di-*p*-toluenosufonyloksy-9,10-anthraquinone and excess of 2-(methylamino)ethanol, dimethylamine and diethylamine, in toluene in high temperature, obtaining 65%, 48%, and 72% yields for derivatives (1), (2), (3) respectively. In case where diethylamine and 2-(methylamino)ethanol were used in equimolar rate to 1,4-di-*p*-toluenosufonyloksy-9,10-anthraquinone, the derivatives (4) and (5) were obtained with 82% and 70% yields respectively.

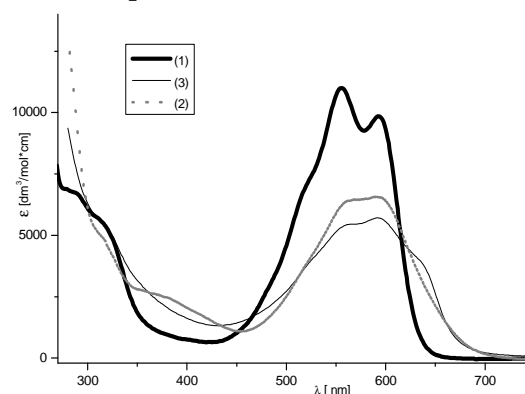
All synthesized compounds were purified using column chromatography. All derivatives were characterized by MS-TOF, NMR and IR spectroscopy.

## Spectrophotometric titrations

All spectrophotometric measurements were performed on Perkin Elmer Lambda 650. All measurements were carried out in acetonitrile. Acid-base titration were carried out in acetonitrile:methanol (9:1) mixture. The pH value was obtained by potentiometric titrations using microtitration automatic system Cerko-Lab. The pH glass-electrode was calibrated on the acetonitrile:methanol (9:1) mixture with method using 2,6-dinitrophenol and its tetrabutylammonium salt. For the evaluation of electrode parameters the STOICHIIO version CVEQUID software was used [7]. In acid-base titrations the compound was dissolved in methanesulfonic acid ( $\text{CH}_3\text{SO}_3$ ) solution (in acetonitrile) and titrated by NaOH base (in methanol). The  $\text{pK}_a$  values were obtained by calculations using Origin Lab software. The separation of bands in absorption spectra and determination the position of those bands were performed by Spectra DataLab software (A.O. Doroshenko 2006).

## 3. Results and discussion Spectral characterization

Anthraquinone derivatives are used to create optical chemical sensors.



**Fig. 2.** Absorption spectra of (1), (2) and (3)

In visible region is observed strong bands which intensity and position strongly depends on the position of the substituent (1, 4, 5 and 8) of anthraquinone ring [1,2].

The presence of hydroxyl and amine substituents near carbonyl group of anthraquinone moiety increase the complexometric properties toward to selected metal ions.

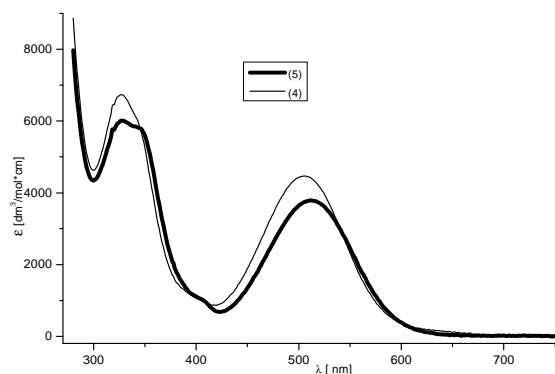


Fig. 3. Absorption spectra of (4) and (5)

For derivatives (1), (2) and (3) is observed absorption  $\pi \rightarrow \pi^*$  type bands in range 220-400 nm and  $n \rightarrow \pi^*$  type bands in region 400-700 nm. For (4) and (5) the  $n \rightarrow \pi^*$  bands are in the region 450-600 nm. For derivatives containing two tertiary nitrogen substituents is observed vibroelectronic band in visible region. This band is not observed for the compounds (4) and (5).

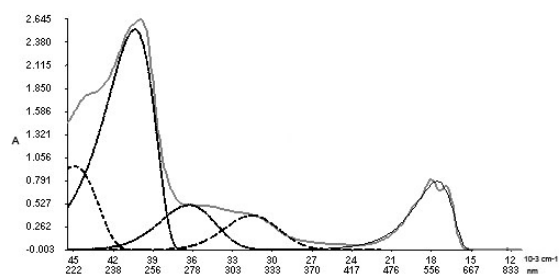


Fig. 4. Absorption spectra for (1) with separated bands

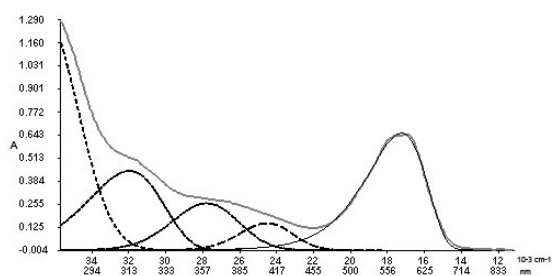


Fig. 5. Absorption spectra for (2) with separated bands

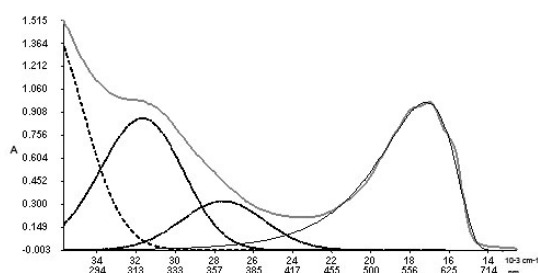


Fig. 6. Absorption spectra for (3) with separated bands

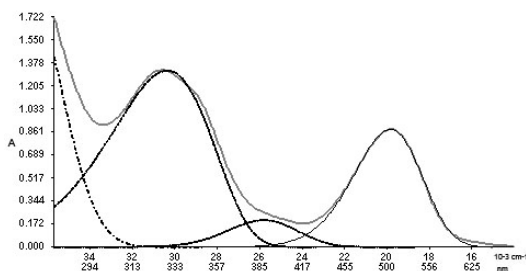


Fig. 7. Absorption spectra for (4) with separated bands

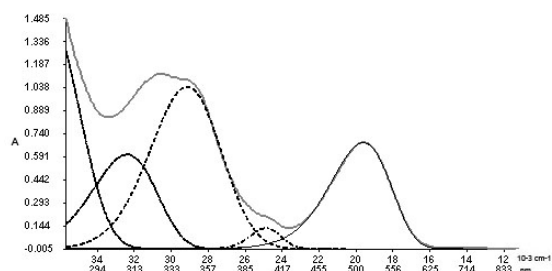


Fig. 8. Absorption spectra for (5) with separated bands

The presence of two tertiary nitrogens affects the separation of vibronic states of the molecule. To determine the number, position (Tab. 1) and real shape of each

band deconvolution method was used (Fig. 4-8).

**Table 1**  
Position of separated bands

(1)		(2)		(3)	
$cm^{-1}$	nm	$cm^{-1}$	Nm	$cm^{-1}$	nm
17550	570	17250	580	17190	582
31530	317	24530	408	27560	363
36290	276	27790	360	31680	316
40390	248	31980	313	36890	271
44950	222	36740	272		

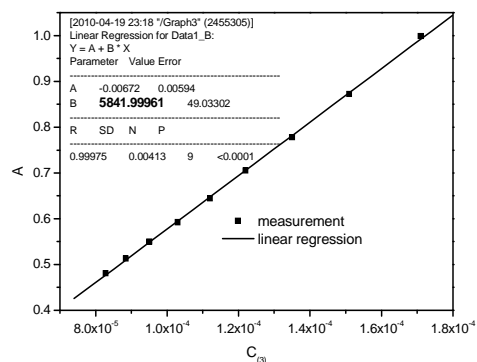
(4)		(5)	
$cm^{-1}$	nm	$cm^{-1}$	nm
19850	504	19600	510
25810	387	24870	402
30370	329	29140	343
37540	266	32400	309
		37020	270

The numbers marked in Table 1 refers to the position of the band in the visible region which decide upon the hue of each compound (Tab. 2). For compounds (2) and (3) is observed a bathochromic shift (respectively 360  $cm^{-1}$  and 300  $cm^{-1}$ ) in relation to compound (1) and also for (5) in relation to (4) (250  $cm^{-1}$ ). Those shifts are followed by change of colour for these derivatives (Tab. 2).

**Table 2**  
The hue of different 1,4-anthraquinone derivatives

Compound	Hue in acetonitrile
(1)	Violet
(2)	Blue
(3)	Blue
(4)	Pink-red
(5)	Pink

The molar absorption coefficient  $\epsilon$  was estimated for each compound (Tab. 3). At the same time linearity of absorbance against used concentration was checked (Fig. 9).



**Fig. 9.** Absorbance against concentration dependence for (3)

The highest molar absorption coefficient is for the compound (1) and the lowest for (5) (Tab. 3). The band in the visible region of the absorption spectrum of derivatives containing tosyl group (-OTs) has lower intensity (Fig. 3).

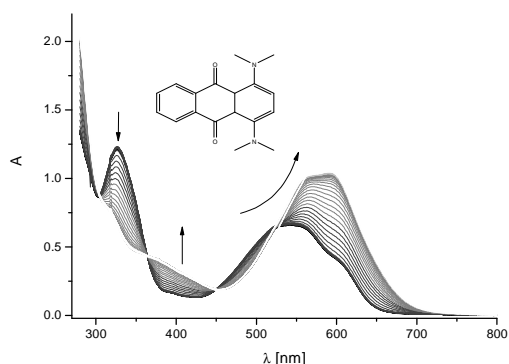
**Table 3**  
Values of molar absorption coefficient for 1,4-anthraquinone derivatives

Compound	$\log \epsilon_{max}$
(1)	4.04
(2)	3.84
(3)	3.77
(4)	3.65
(5)	3.58

### 3.1 Acid-base properties

Acid-base properties of a molecule provides useful and important information about its behavior and form in different environments. It enables to predict the form of compound and provides information necessary for biological experiments. Therefore the  $pK_a$  values was established for each investigated derivative.

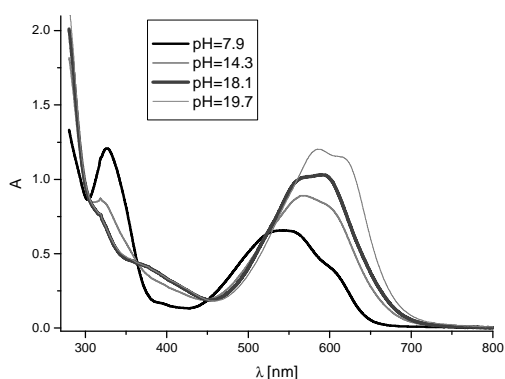
To obtain the  $pK_a$  values for 1,4-anthraquinone derivatives spectrophotometric titration combined with potentiometry was used as described in Sec. 2.2. These values give a relative measure of the basicity of the substituents.



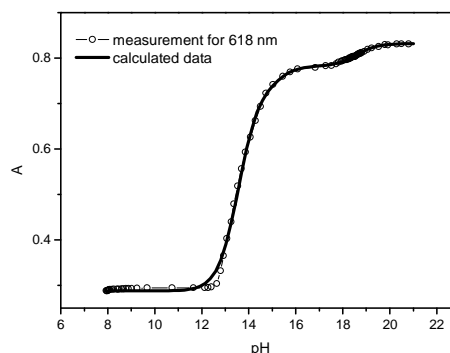
**Fig. 10.** Titration spectra for (2) in mixture acetonitrile:methanol (9:1) over the pH range 7.9 – 19.7. For titration conditions see Sec. 2.2

To establish the acid-base properties of investigated compounds following graphic methods were used:

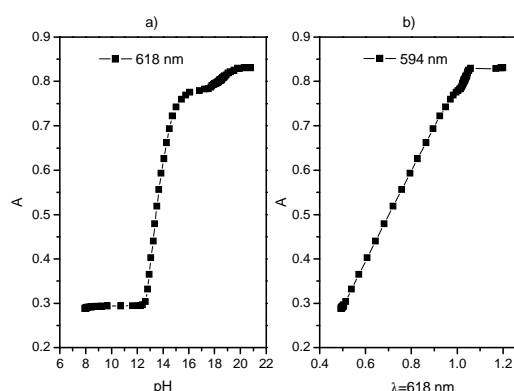
- analysis of titration spectra with respect to isosbestic points,
- analysis of spectrophotometric titration curves  $A$  vs.  $pH$  with respect to inflection points, maxima and minima,
- establishment of linearity with respect to absorbance diagrams ( $A$ -diagrams)  $A_{\lambda 1}$  vs.  $A_{\lambda i}$ .



**Fig. 11.** Titration spectra for (2) over the pH range 7.9 – 19.7. For titration conditions see Sec. 2.2



**Fig. 12.** Fitting of calculated data to measurement at  $\lambda=618$  nm



**Fig. 13.** Spectrometric titration curves: a)  $A$  vs  $pH$  curve at  $\lambda=618$  nm, b)  $A$ -diagram for (2) (for titration conditions see Sec. 2.2)

The number of straight lines in  $A$ -diagrams (cf. Fig. 13 b) inform about the number of existing equilibria. This information is usually also visible in spectrometric titration curve  $A$  vs.  $pH$  (cf. Fig. 13 a). Isosbestic points on the other hand are points where all existing forms of the molecule have the same molar absorption coefficient  $\epsilon$ . When this point is vanishing during titration, it can tell us, that there are more complex equilibria.

**Table 4**  
 $pK_a$  values for 1,4-anthraquinone derivatives

Compound	$pK_{a1}$	$pK_{a2}$
(1)	$4.82 \pm 0.89$	$17.76 \pm 0.61$
(2)	$13.56 \pm 0.02$	$18.41 \pm 0.04$
(3)	$7.84 \pm 0.04$	$18.53 \pm 0.06$
(4)	$8.97 \pm 0.03$	$15.91 \pm 0.30$
(5)	$10.90 \pm 0.01$	$14.55 \pm 0.02$

High values of the  $pK_a$  are consistent with the basicity of the solvent and with its capability of solvating the compounds [2]. The  $pK_a$  values suggest that the compounds containing two tertiary nitrogens have higher value of the variable  $pK_{a2}$  than those with one such substituent (about 3 units). The basicity of such compound is higher. The number of substituents containing tertiary nitrogen affects the basicity of the compound.

#### 4. Conclusions

The purpose of the present investigation was to determine the influence of different substituent on spectroscopic and acid-base properties of 1,4-anthraquinone derivatives. Particularly the point of interest was to obtain  $pK_a$  values for each compound and define the role of the tertiary nitrogen group ( $-NH_2$ ) in spectral and acid-base properties of 1,4-anthraquinone derivatives.

In line with this goals spectrophotometrical acid-base titrations as well as calculations of  $pK_a$  values using Origin Lab software were carried out.

The absorption spectra of all compounds were determined. Also separation of the bands in every spectrum and determination of its position and shape was performed.

The presence of two tertiary nitrogen groups affects the electron structure of the molecule and effects with vibroelectronic bands in visible region. The vibration states are separated more than for derivatives with only one  $-NH_2$  group. The presence of different substituents in location 1,4 changes the position of the band in visible regions which effects in colour change. The number of these groups decides about the basicity of derivative, as the study shows.

**Acknowledgement.** Work supported by BW 8210-5-0472-0.

#### REFERENCES

- [1] H. Pal, D. K. Palit, T. Mukerjee, J. P. Mittal, *J. Photochem. Photobio. A*, 62 (1991) 183.
- [2] A. Bogdańska, L. Chmurzyński, T. Ossowski, A. Liwo i D. Jeziorek, *Anal. Chim. Acta*, (1999) 402, 339.
- [3] N.S. Allen, G. Pullen, M. Shah, M. Edge, D. Holdsworth, I. Weddell, R. Swart, F. Catalina, *J. Photochem. Photobio. A*, 91 (1995) 73-79.
- [4] T. Philipova, C. Ivanova, Y. Kamdzhilov, M.T. Molina, *Dyes and Pigments* 53 (2002) 219-227.
- [5] T. Ossowski, J. Kira, D. Rogowska, H. Warmke, J. Młodzianowski, *J. Chem. Soc., Dalton Trans.*, (2000) 689-696.
- [6] K. Dzierzbicka, P. Sowiński, A. M. Kołodziejczyk, *J. Pept. Sci.*, (2006) 12: 670-678
- [7] J. Kostrowicki, A. Liwo. *Talanta*, 37 (1990) 645.