

Scientific paper

Investigation of the Acid-base Properties of 2-[2-(4-Methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium Reagent

Vasil Andruch,^a Ioseph S. Balogh,^b Yaroslav R. Bazel,^a Ferenc Billes,^c Mihály Kádár,^d Roland Karosi,^e Gyula Parlagh,^c József Posta,^e András Simon,^d Rastislav Serbin,^{a,*} Marcel Torok^a

^a Department of Analytical Chemistry, P. J. Šafárik University, Moyzesova 11, SK-04154 Košice, Slovak Republic,

* Corresponding author: E-mail: rasto00@yahoo.com

^b Department of Chemistry, University of Nyíregyháza, Sóstói út 31/b, Nyíregyháza, Hungary, baloghj@nyf.hu

^c Department of Physical Chemistry, Budapest University of Technology and Economics, Műegyetem rkpt. 3, H-1521 Budapest, Hungary, fbilles@mail.bme.hu

^d Department of General and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, H-1111 Budapest, Hungary, andras.simon@mail.bme.hu

^e Department of Analytical Chemistry, University of Debrecen, Egyetem tér 1, Debrecen, Hungary, postaj@tigris.unideb.hu

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Abstract

The acid-base properties of 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium dye were investigated. The reagent exists in a reactive single charged form over a wide range of acidity, from pH 8 to $-2.5 H_0$. The optimum analytical wavelength of the single charged form is 412 nm, where the molar absorptivity is $4.06 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Mechanisms of protonation and hydrolysis were discussed. The results suggest the applicability of the dye as an effective analytical reactant. Quantum chemical calculations of the structural and spectral properties of the dye were also carried out.

Keywords: 2-[2-(4-Methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium; spectrophotometry; acid-base properties

1. Introduction

Complex-forming reagents are widely used in a variety of analytical techniques. For the continued development of novel analytical procedures, the investigation of new reagents is always necessary. The study of the acid-base and spectral properties of complex-forming reagents allows for simplification in choosing the appropriate reaction conditions and better application of these reagents in analytical chemistry since acid-base properties have a significant influence on the abilities of dye reagents to form and extract complexes.

The application of complex formation in analytical chemistry is based on the different abilities of analytes to react with various complex-forming reagents. The com-

plex formation depends on experimental conditions (the concentration of reagents, the acidity of medium, etc.) and on the nature of the complex-forming reagent. Therefore, the choice of appropriate experimental conditions and a suitable complex-forming reagent enables the use of the complexation process for the separation, preconcentration and determination of elements. Some useful information about element complexes can be found in the work of Greenwood and Earnshaw.¹ The trends in organic complex-forming reagents were discussed in the work of Prasad Rao et al.²

Many articles have been devoted to the application of complex-forming reagents for the separation, preconcentration and determination of certain elements, such as: copper(II),³ arsenic(III),⁴ palladium(II),⁵ lead,⁶ gold,⁷

vanadium(V),⁸ tellurium(IV),^{9,10} bismuth(III),¹¹ rhenium,¹² manganese,^{13,14} nickel,¹⁵ silver¹⁶ and others.^{17–23} The application of various complexes in spectrophotometric analysis has been discussed in a series of books and reviews.^{24,25}

The reactivity and extraction abilities of basic dye reagents depend on the acidity of the medium used,^{26,27} the concentration of the dye,^{28,29} the contents of the aqueous phase,³⁰ and ion strength and temperature. Oxidation-reduction processes, through which colourless forms of dye often originate, also influence the state of basic dye reagents. The spectral characteristics of basic dye reagents also change depending on the nature of the solvent.³¹

The reaction of complexes with basic dye reagents, as a rule, occurs in the aqueous phase. Therefore, for the evaluation of the extraction capabilities of basic dye reagents, for ascertaining the extraction mechanism and for finding out the optimal conditions for determination, it is necessary to obtain information about the actual state of the reagents in solution. For this reason, the acid-base properties of some basic dyes were studied.^{32–35}

The aim of this work was the study of the acid-base and spectral properties of 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium (**I**) (Figure 1) and the determination of its main analytical characteristics, such as molar absorptivity and optimum wavelength. The investigated reagent was previously used for the determination of chromium(VI).^{36,37}

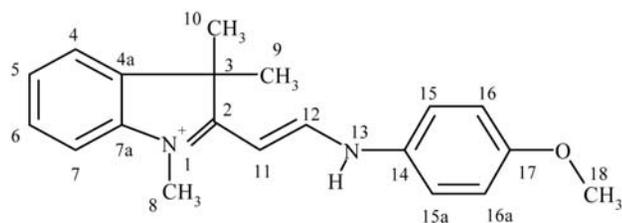


Figure 1. The structure of **I**.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade and double distilled water was employed throughout the investigation. **I** was purified by recrystallization from methanol, and a 1×10^{-3} mol dm⁻³ aqueous solution of **I** was prepared by dissolving a precise amount of **I** in water. The acidity of the medium was then adjusted by the addition of sulphuric acid, sodium hydroxide or (CH₃COOH–NH₄OH) buffer solutions.

2.2. Apparatus

Absorption spectra in the 220–600 nm region were recorded using a Unicam model 400 double beam UV-

VIS scanning spectrophotometer with matched quartz cells of 10 mm path length.

FAB MS spectra (positive mode) were recorded on a MAT 312 machine equipped with an ION TECH FAB system and a MASPEC II³² (Mass Spectrometry Services Ltd.) data system. The samples were dissolved in NOBA (3-nitrobenzyl alcohol) or glycerol and argon was used as the bombarding gas.

NMR spectra were recorded with a Bruker Avance DRX-500 spectrometer. Chemical shifts are given on the δ -scale and were referenced to a solvent signal (CDCl₃, 300 K, $\delta_C = 77.23$ and $\delta_H = 7.27$). Unambiguous ¹H and ¹³C NMR assignments were achieved through ¹H, ¹³C, APT, HMQC, COSY, ROESY (mixing time: 350 ms) and HMBC experiments. The HMBC measurement was optimized for a 7.5 Hz long-range coupling constant.

The pH values of the solutions were measured using a digital laboratory pH-meter (OP-211/1 Radelkis, Hungary) with a glass electrode.

3. Results and Discussion

3.1. Investigation of Structure

Mass spectra were measured in 3-nitrobenzyl alcohol (NOBA) and in glycerol. In NOBA an intensive molecular peak was observed at $m/z = 307$ and a smaller signal at $m/z = 292$ (M–CH₃). Thus, the molecular weight of **I** should be 307. Since NOBA itself has a minor signal at $m/z = 307$, the measurement was repeated in glycerol. The same two signals were observed, thus confirming the molecular weight of the cation as 307.

The ¹H and ¹³C NMR spectra (Figures 2 and 3) of **I** were recorded. The ¹H and ¹³C chemical shifts, multiplicities, and characteristic H,H–COSY, H,H–ROESY, and H,C–HMBC correlations of **I** are summarized in Table 1. The starting points of structural elucidation were the methyl signals in positions 9 and 10. Identification of these geminal methyl groups was unambiguous owing to their mutual HMBC correlation. The HMBC spectra (Figure 5) of H₃–9 and H₃–10 identified the C–2, C–3 and C–4a carbon atoms. C–3 gave a correlation with a doublet signal at 7.32 ppm (H–4). Using the COSY spectrum, we were able to identify the aromatic CH-units from H–4 to H–7. The HMBC spectra of H–4, H–6 and H₃–8 identified C–7a. H₃–8 gave a cross peak with C–2 allowing us to close the five membered-ring.

The COSY spectrum (Figure 4) of H–12 identified an overlapping signal at 7.27 ppm (H–11). H–12 showed an HMBC correlation to C–14. Doublets at 7.40 ppm and 6.86 ppm in the HMBC spectra correlated with C–14. Their integral value (2) proved the existence of a 1,4-disubstituted benzene ring. The assignment of these two doublets to position 15/15a and 16/16a was achieved by the ROESY (Figure 6) cross peak between H–12 and the signals at 7.40 ppm (H–15/15a). The HMBC correlation

of the methyl signal at 3.77 ppm to C-17 and the ROESY cross peak between H-16/16a and the methyl signal at 3.77 ppm justified the para-substitution of a methoxy group.

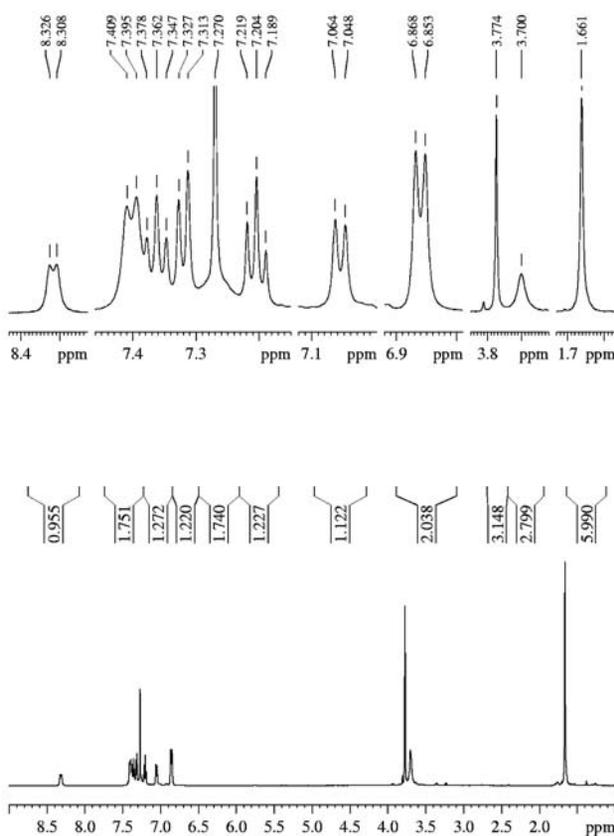


Figure 2. The ^1H spectrum of **I**.

Table 1. ^1H and ^{13}C NMR chemical shifts, multiplicities, and characteristic H,H-COSY, H,H-ROESY, and H,C-HMBC correlations for **I**.

| No ^a | ^1H NMR (ppm) | ^{13}C NMR (ppm) | m, J (Hz) | H,H-COSY | H,H-ROESY | H,C-HMBC |
|-----------------|------------------------|---------------------------|-----------|-------------|-------------|-------------------------|
| 2 | – | 176.2 | – | – | – | – |
| 3 | – | 48.8 | – | – | – | – |
| 4a | – | 140.2 | – | – | – | – |
| 4 | 7.32 | 122.0 | d; 7.4 | 7.20 | 7.20, 1.66 | 143.1, 128.9, 48.8 |
| 5 | 7.20 | 124.9 | t; 7.5 | 7.36, 7.32 | 7.36 | 143.1 (w), 140.2, 110.5 |
| 6 | 7.36 | 128.9 | t; 7.7 | 7.20, 7.055 | 7.20, 7.055 | 143.1, 122.0, 110.5 (w) |
| 7 | 7.055 | 110.5 | d; 7.8 | 7.36 | 7.36 | 143.1 (w), 140.2, 124.9 |
| 7a | – | 143.1 | – | – | – | – |
| 8 | 3.70 | 31.9 | s | – | – | 176.2, 143.1 |
| 9 | 1.66 | 29.4 | s | – | 8.32, 7.32 | 176.2, 140.2, 48.8 |
| 10 | 1.66 | 29.4 | s | – | 8.32, 7.32 | 176.2, 140.2, 48.8 |
| 11 | 7.27 ^b | 93.5 | – | 8.32 | – | – |
| 12 | 8.32 | 151.2 | d; 8.9 | 7.27 | 7.40, 1.66 | 133.2 (w) |
| 14 | – | 133.2 | – | – | – | – |
| 15/15a | 7.40 | 120.2 | d; 7.8 | 6.86 | 8.32, 6.86 | 158.4, 120.2 |
| 16/16a | 6.86 | 115.1 | d; 8.0 | 7.40 | 7.40, 3.77 | 158.4, 133.2, 115.1 |
| 17 | – | 158.4 | – | – | – | – |
| 18 | 3.77 | 55.8 | s | – | 6.86 | 158.4 |

^a Serial numbers of the skeletal atoms.

^b Overlapping with solvent.

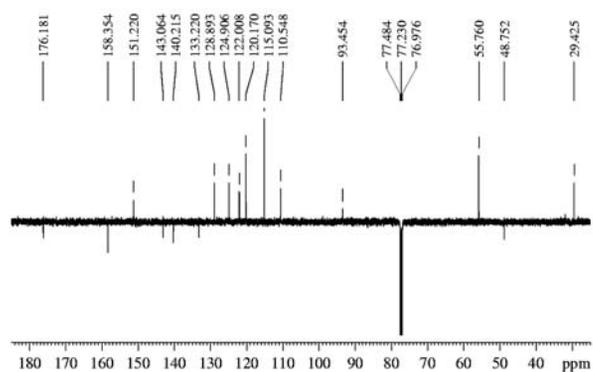


Figure 3. The ^{13}C APT spectrum of **I**.

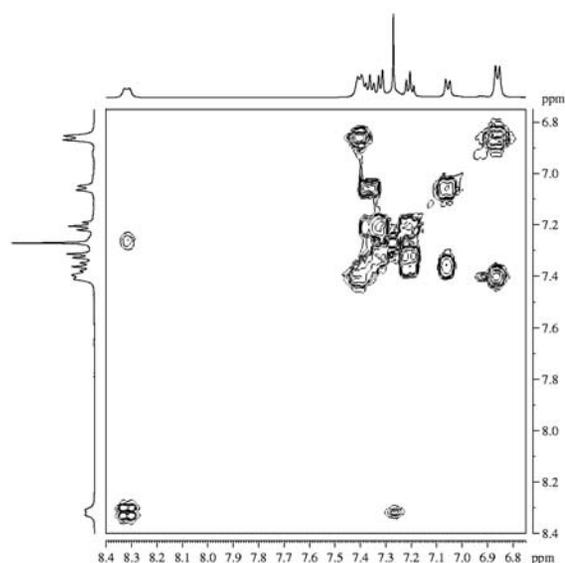


Figure 4. The COSY spectrum of **I**.

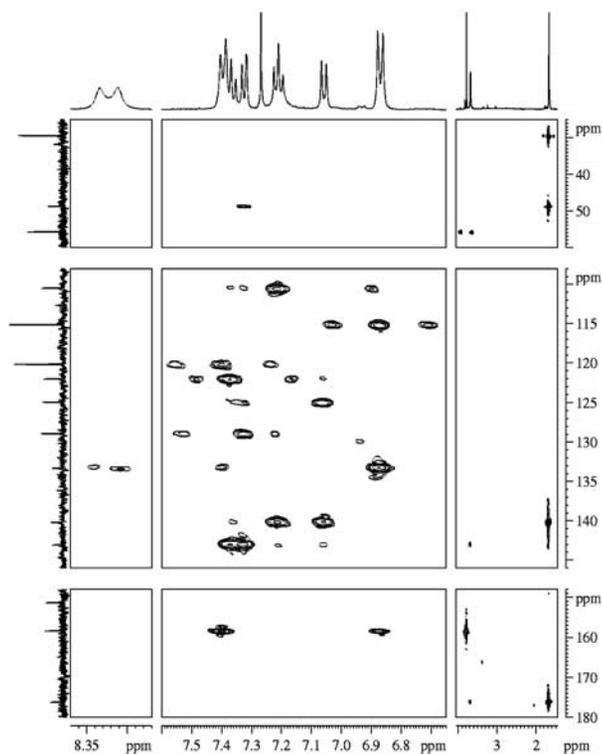


Figure 5. The HMBC spectra of **I**.

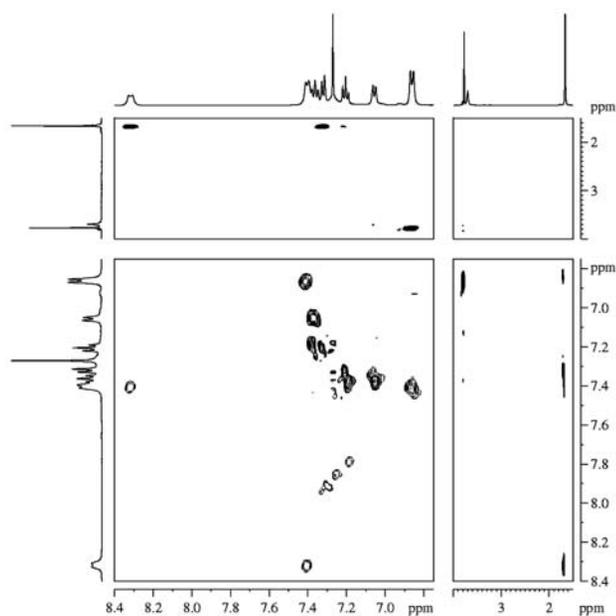


Figure 6. The ROESY spectrum of **I**.

3. 2. Investigation of Acid-base Properties

The investigation of the acid-base properties of **I** was realized in the range from pH 14 to the concentration of H_2SO_4 up to 14.3 mol dm^{-3} . The reagent forms ionic associates in the single positive charged form. Therefore,

the most practical interest appears in the range of medium acidity at which this form predominates. As follows from the absorption spectra (Figure 7), the single charged form of **I** predominates in a wide range of acidity from pH 8 to -2.5 H_0 (Figure 8). The optimum analytical wavelength of the single charged form is at 412 nm, where molar absorptivity is $4.06 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

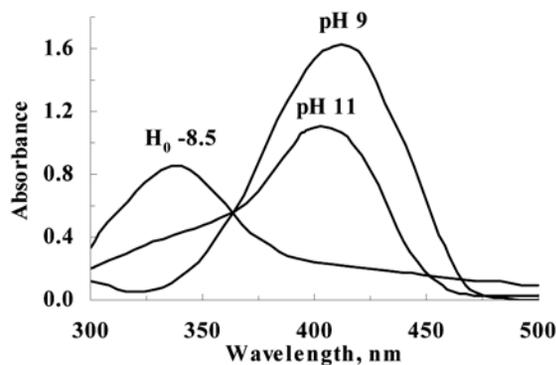


Figure 7. Absorption spectra of **I** at different acidities, $4 \times 10^{-5} \text{ mol dm}^{-3}$ of **I**, $l = 10 \text{ mm}$.

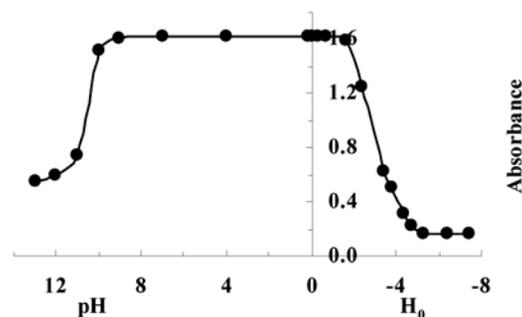
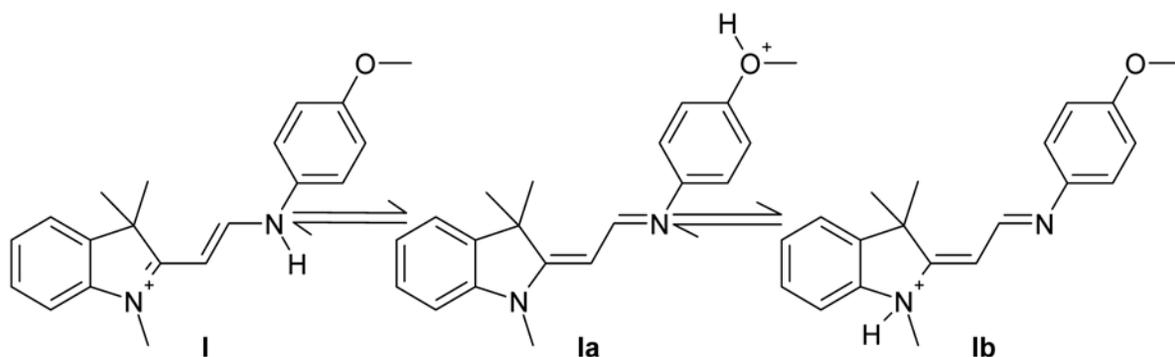


Figure 8. Influence of the medium acidity on the absorbance of **I**, $4 \times 10^{-5} \text{ mol dm}^{-3}$ of **I**, $l = 10 \text{ mm}$, $\lambda = 412 \text{ nm}$.

At $\text{pH} > 9$, the compound begins to hydrolyse, which causes a lowering of the absorbance value at $\lambda = 412 \text{ nm}$. This process is accompanied by a stepwise shift in absorption maximum to the region of shorter wavelengths. The hydrolysis of the compound is reversible. By increasing the acidity of the medium, the absorbance at 412 nm was lowered and a new peak was observed at 336 nm. The lowering of the absorbance begins to appear at very high concentrations of H_2SO_4 . Therefore, Hammett's function of acidity H_0 was used in place of pH.³⁸ This reaction is not reversible, suggesting that the decomposition of the compound occurred, instead of the protonation.

A theoretical study of the spectral and chemical properties of **I** was conducted with quantum chemical calculations using the DFT method with the B3LYP functional and the 6-31G(d) basis set.³⁹ The first step was



Scheme 1. Tautomeric equilibria of **I**.

geometry optimisation and calculation of the electronic properties of the three possible tautomers, **I**, **Ia**, **Ib** (Scheme 1). We assume the rapid exchange of a proton between heteroatoms N1, N13 and O. Calculations were performed for these tautomers in the gas phase and in a polar medium (PCM model with a predefined parameter for water as solvent). Results showed a strong preference for tautomer **I**, which is more stable in all cases despite the stabilisation effect of the polar medium on **Ia** and **Ib** (Table 2).

The preference for tautomer **I** can be shown by comparing the electronic absorption spectra, which were calculated for each structure in the gas phase and in the polar medium using the TDDFT method and the B3LYP/6-31G(d) basis set. The theoretically calculated maximum absorbance at 410 nm for the polar medium (Table 2) is consistent with the experimental value, while values for **Ia** and **Ib** are considerably lower (383 nm and 372 nm).

The theoretical investigation of the acid-base properties was realized by studying a map of electrostatic potential (MEP) and by natural bond orbital (NBO) analysis. Analysis of the MEP and the charge distribution of **I** showed the theoretical possibility of its protonation and the formation of cations **IIa**, **IIb** and **IIc** (Scheme 2). Energy and electronic absorption spectra for the optimised structure of these cations as isolat-

ed structure and in polar medium were then calculated (Table 2). Results showed the great sensitivity of their stability on the solvent effect. The most stable cation as isolated structure and in polar solvent is **IIa** (with protonation on the oxygen atom of the methoxy group). According to our model, the polar medium has a strong stabilization effect on cation **IIb** and the difference between the energy of **IIa** and **IIb** is only 4.14 kJ/mol. Therefore, the presence of **IIb** in solution could also be expected. After the protonation of **I** at N13 atom, the breaking of the bond between N13 and C12 in **IIb** can proceed very easily. Such two-step process could explain the irreversible dissociation of **I** in a strongly acidic medium.

In basic solution, according to the analysis of the charge distribution and coefficients of LUMO, orbital attack of the hydroxyl group at position 2 of the indole ring or at atom C12 could be expected. In both cases the result is a decrease in the conjugation between the indole ring and the phenyl group and a shift in the maximum absorbance in the UV spectra to the shorter wavelengths.

The maximum positive net charges under the skeletal atoms are found on the C2 atom of the indole ring and on the C12 atom. It is thought that this part of the molecule could be directly responsible for the ion association of the given dye with the anion being analytically determined.

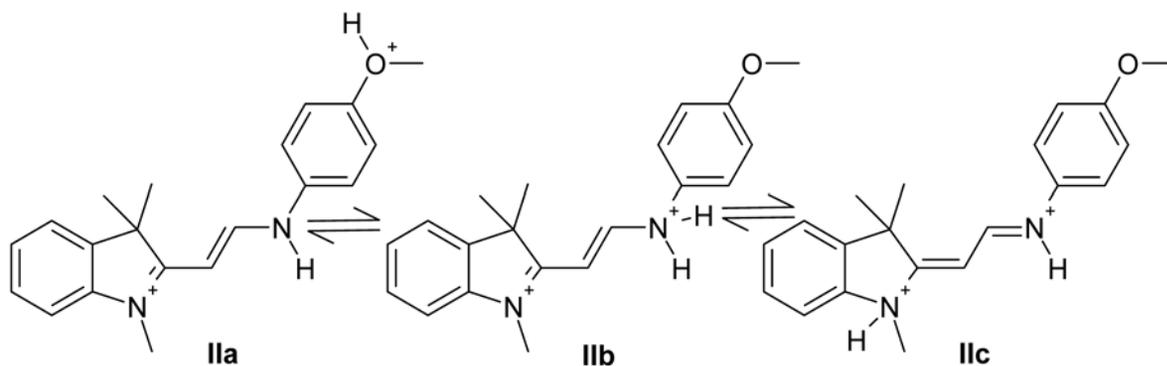
Table 2. Calculated total energies and UV absorption maxima of the investigated structures^a.

| Structure | Gas phase | | | In solvent ^b | | |
|------------|--------------------------|---------------------------|------------------------|--------------------------|---------------------------|------------------------|
| | E ^c [hartree] | E _{rel} [kJ/mol] | UV _{max} [nm] | E ^c [hartree] | E _{rel} [kJ/mol] | UV _{max} [nm] |
| I | -960.1113610 | 0.00 | 429 | -960.1818585 | 0.00 | 410 |
| Ia | -960.0225070 | 233.29 | 406 | -960.1298824 | 136.46 | 383 |
| Ib | -960.0508140 | 158.97 | 403 | -960.1320537 | 130.76 | 372 |
| IIa | -960.3321890 | 0.00 | 418 | -960.5707660 | 0.00 | 390 |
| IIb | -960.3193670 | 33.66 | 692 | -960.5691890 | 4.14 | 506 |
| IIc | -960.3107380 | 56.32 | 502 | -960.5552075 | 40.85 | 440 |

^a Relative energies related to the minimal energy structure of **I** and **II**, respectively.

^b PCM model, water, $\epsilon = 78.39$.

^c Total electronic energy with correction to zero point energy ($E_0 + E_{ZPE}$).



Scheme 2. Tautomeric equilibria of the protonated form II.

4. Conclusion

The acid-base properties of 2-[2-(4-methoxy-phenyl-amino)-vinyl]-1,3,3-trimethyl-3H-indolium dye were investigated. The reagent exists in a reactive single charged form over a wide acidity range, from pH 8 to -2.5 H_0 . The optimum analytical wavelength of the single charged form is 412 nm, where the molar absorptivity is $4.06 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The mechanisms of protonation and hydrolysis were discussed. It turned out that the applied methods (MS, NMR and quantum chemical calculations) are very good tools for searching of the analytically active form of the dye. The results suggested the applicability of the dye as an effective analytical reactant.

5. Acknowledgements

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Povzetek

V prispevku so podane kislinsko-bazične lastnosti 2-[2-(4-metoksifenilamino)-vinil]-1,3,3-trimetil-3*H*-indolnega barvila kot reagenta. Ugotovljeno je bilo, da obstaja v reaktivni, enkrat nabiti obliki v širokem območju, od pH 8 do $-2.5 H_0$. Optimalna analitska valovna dolžina takšne oblike barvila je pri 412 nm, z molarno absorptivnostjo $4.06 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Predstavljeni so različni mehanizmi protonacije in hidrolize barvila. Rezultati raziskave nakazujejo možno uporabo barvila kot učinkovitega analitskega reaktanta. Pri analizi so bili uporabljeni tudi kvantno-kemijski izračuni strukture in spektroskopskih lastnosti barvila.