

PHYSICAL METHODS
OF INVESTIGATION

Electronic Structure and Electrooptical Properties of Radicals Formed upon Reduction of *N*-Alkyl 4,4'-Bipyridylium Salts

V. V. Minin^{a,*}, M. I. Zakirov^b, N. N. Efimov^a, P. V. Mel'nikov^c, E. L. Nodova^d,
B. I. Shapiro^c, and V. M. Novotortsev^a

^aKurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia

^bTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia

^cLomonosov Moscow State University of Fine Chemical Technology, Moscow, 119571 Russia

^dInternational University of Nature, Society, and Man "Dubna," Moscow, 141980 Russia

*e-mail: minin@igic.ras.ru

Received October 3, 2017

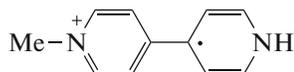
Abstract—*N*-Alkyl 4,4'-bipyridylium salts were synthesized and characterized. Cyclic voltammetry investigation showed that monosubstituted 4,4'-bipyridylium salts are prone to reversible single-electron reduction. The formal redox potentials vs. a saturated silver chloride electrode were determined for different potential sweep rates. High-resolution ESR spectra of the radical cations formed upon the reduction of *N*-substituted 4,4'-bipyridylium salts in acid media were measured and interpreted. The substituent structure and the type of anion in the molecule have a considerable effect on the spin density distribution, current–voltage characteristics, and electrooptical properties. The applicability of monosubstituted 4,4'-bipyridylium salts as photoelectrochromic compounds was studied.

DOI: 10.1134/S0036023618060189

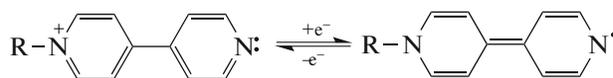
Disubstituted 4,4'-bipyridylium salts (viologens) are widely used as herbicides [1], electro- [2] and photochromic [3] compounds, and thin-film catalysts for fuel cells [4]. Conversely, monosubstituted 4,4'-bipyridylium salts have not aroused much interest, but have been used as intermediates for the preparation of unsymmetrical viologens.

It is known that reduction of viologens affords radical cations (RC) that exhibit chromism. This term stands for the reversible color change under the action of electric current or on exposure to light or electron beam. If the color changes under the action of ultraviolet radiation and changes back on exposure to visible light, this phenomenon is called photochromism. If the color change is induced by electron beam, this is cathodochromism, and the electric field-induced color change is called electrochromism.

Study of monosubstituted bipyridylium salts shows that the radicals resulting from reduction of the initial salts tend to form chelates. The formation of these chelates has been described in the literature [5]. The electrochemical reduction of *N*-methyl-4,4'-bipyridylium in acidic aqueous solutions (pH 2–5.3) is accompanied by protonation of the unsubstituted nitrogen to give intensely colored RC [6]:

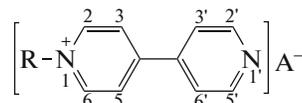


In this communication, we report the synthesis of a number of monosubstituted 4,4'-bipyridylium salts. The radical cations derived from monosubstituted 4,4'-bipyridylium salts were studied and characterized by electron spin resonance (ESR). The radical cations were obtained by electro- and photochemical reduction.



EXPERIMENTAL

The monoalkyl 4,4'-bipyridylium salts of the general formula



(**1**, **2**, R = CH₃, A = I, PF₆; **4**, **5**, R = CH₂–CH=CH₂, A = Br, PF₆; **6**, **7**, R = CH₂C₆H₅, A = Cl, PF₆) for this study were prepared by procedures described below. The products were characterized by ¹H NMR spectroscopy, elemental analysis, and MALDI mass spectrometry.

In order to increase the solubility of monoalkyl 4,4'-bipyridylium salts in less polar solvents, the halide anion was replaced by the hexafluorophosphate anion

via addition of an aqueous solution of ammonium hexafluorophosphate to a stirred aqueous solution of bipyridylum salt followed by collection of the precipitate on a glass filter.

1-Methyl-4,4'-bipyridylum iodide. 4,4'-Bipyridine (6.24 g, 40 mmol) and iodomethane (2.73 g, 44 mmol) were stirred at room temperature in acetone for 24 h. The precipitate was collected on a glass filter and recrystallized from an isopropyl alcohol–water mixture to give a yellow powder. The yield was 75%.

^1H NMR (500 MHz, D_2O as the solvent, and TMS as the reference) (δ): 8.95 (d, 2H); 8.84 (d, 2H); 8.75 (d, 2H); 7.99 (d, 2H); 4.39 (s, 3H).

For $\text{C}_{11}\text{H}_{11}\text{N}_2\text{I}$, anal. calcd. (%): C, 44.31; H, 3.72; N, 9.40; I, 42.57.

Found (%): C, 4.25; H, 3.76; N, 9.36; I, 42.61.

m/z : 171.

1-Allyl-4,4'-bipyridylum bromide. 4,4'-Bipyridine (4.68 g, 30 mmol) and allyl bromide (3.63 g, 30 mmol) were stirred at room temperature in acetone for 24 h. The precipitate was collected on a glass filter and recrystallized from isopropyl alcohol to give a pink powder. The yield was 79%.

^1H NMR (500 MHz, D_2O as the solvent, and TMS as the reference) (δ): 8.88 (d, 2H); 8.65 (d, 2H); 8.31 (d, 2H); 7.81 (d, 2H); 6.10 (m, 1H); 5.48 (m, 2H); 5.20 (d, 2H).

For $\text{C}_{13}\text{H}_{13}\text{BrN}_2$, anal. calcd. (%): C, 56.34; H, 4.73; N, 10.10; Br, 28.83.

Found (%): C, 56.27; H, 4.79; N, 10.04; Br, 28.88.

m/z : 197.

1-Benzyl-4,4'-bipyridylum chloride. 4,4'-Bipyridine (4.68 g, 30 mmol) and benzyl chloride (3.81 g, 30 mmol) were refluxed in toluene for 4 h. The mixture was cooled and the precipitate was collected on a glass filter and recrystallized from a toluene–isopropyl alcohol mixture to give a white powder. The yield was 50%.

^1H NMR (500 MHz, D_2O as the solvent, and TMS as the reference) (δ): 9.02 (d, 2H); 8.76 (d, 2H); 8.40 (d, 2H); 7.89 (d, 2H); 7.53 (s, 5H); 5.87 (s, 2H).

For $\text{C}_{17}\text{H}_{15}\text{N}_2\text{Cl}$ anal. calcd. (%): C, 72.20; H, 5.35; N, 9.91; Cl, 12.54.

Found (%): C, 72.10; H, 5.40; N, 9.86; Cl, 12.62.

m/z : 247.

The concentration of monosubstituted 4,4'-bipyridylum salts in solutions for photochemical reduction was chosen most often to be around $(1-2) \times 10^{-3}$ mol/L; the solvents were 96% ethanol, acetonitrile, and *N,N*-dimethylformamide (DMF). Solutions of the quaternary bipyridylum salts in the specified solvent were degassed prior to experiments. For removal of atmospheric oxygen, solutions of the samples were frozen by liquid nitrogen directly in the electrochemical cell, evacuated to a residual pressure of 10^{-3} mmHg, and then unfrozen; these operations were

repeated several times until gas evolution was no longer detected. Then the cell was filled with argon.

The radicals were generated by irradiating the samples with a 100 W gas discharge mercury lamp. This induced a change in the solution color, with the ESR signal being increased with increasing color intensity.

The ESR spectra were run on a Bruker E-680X ELEXSYS radiospectrometer at room temperature within 5–10 min after the start of photolysis or mixing of solutions. For increasing the spectrometer resolution, a modulation frequency of 30 kHz was used.

The theoretical simulation of the ESR spectra was carried out using a dedicated Spectrum Analyzer software (P. V. Mel'nikov).

Cyclic voltammograms were measured using an Ekotest-VA voltammetric analyzer manufactured by the LLC Ekonix-Expert. Prior to recording cyclic voltammograms, oxygen was eliminated from the systems by bubbling argon for 5 min. DMF was used as the solvent; 0.15 M tetrabutylammonium bromide served as the supporting electrolyte; and a saturated silver chloride reference electrode was used.

The electrooptical characteristics of DMF solutions of the monosubstituted salts were measured in glass cells (Fig. 1a). An experimental setup was designed to study characteristics of electrochromic devices (Fig. 1b). A direct voltage was applied to sample (3) from power source (4). In the experiment, a light beam from light source (1) having passed through diaphragm (2) was measured with sensor (5) of spectrometer (8) connected to computer (6). The voltage drop in the resistor connected in series with the sample was applied to oscilloscope (7). The resistance of the resistor was adjusted in such a way that it had no noticeable effect on the current through the sample (not more than 10% of the sample resistance). The data recorded by the oscilloscope were used to calculate the dependence of the charge passed through the sample on the coloring and/or bleaching time and electrochromic efficiency. The absorption and transmission spectra were recorded on a USB HR 4000 spectrometer (OceanOptics) (8).

RESULTS AND DISCUSSION

According to cyclic voltammetry data, monoalkyl 4,4'-bipyridylum halide salts are prone to reversible single-electron reduction (Fig. 2). This type of curves is typical of all monosubstituted 4,4'-bipyridylum salts.

According to the Nernst theory [7], the ΔE value for a reversible single-electron electrochemical process should be 59 mV. However, the influence of uncompensated resistance of the solution and other factors leads to increase in ΔE to 60–70 mV, which is similar to the result that we obtained at low sweep rates. It is also known that with increasing sweep rate, ΔE increases (Fig. 2).

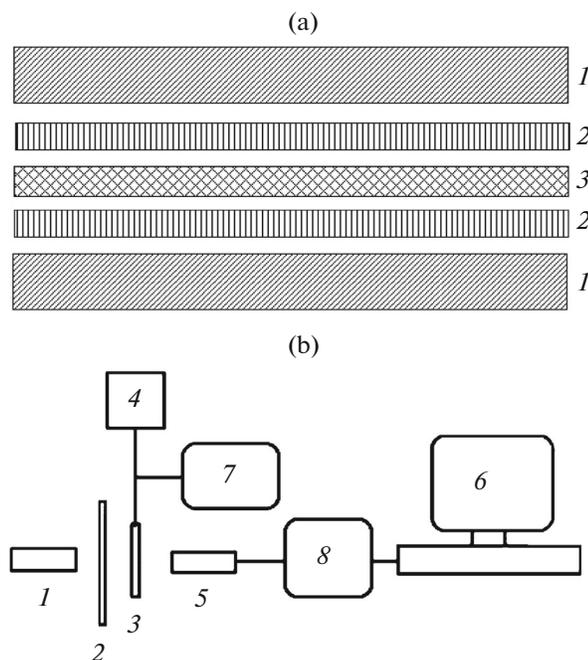


Fig. 1. (a) Structure of the electrochromic cell: (1) glass, (2) transparent conducting indium tin oxide (ITO) layer, (3) EC composition; (b) diagram of the experimental setup for testing EC devices: (1) light source, (2) diaphragm, (3) sample, (4) direct voltage source, (5) spectrometer sensor, (6) computer, (7) oscilloscope, (8) spectrometer.

Table 1 presents the experimental redox potentials of monosubstituted 4,4'-bipyridylium salts. As the anion bulk grows in the series **1** ($A = I$) < **2** ($A = PF_6$), **3** ($A = Br$) < **4** ($A = PF_6$), **5** ($A = Cl$) < **6** ($A = PF_6$), the potential increases. Apparently, this trend is caused by the fact that counter-ion migration slows down as its size increases.

The theoretical simulation of the ESR spectra was carried out using a phenomenological model of the hyperfine structure (HFS). It is a linear combination of Lorentzians corresponding to single spectral transitions taking account of spectral density components for dynamic perturbations.

For developing an adequate model for reliable HFS simulation, one should know the limiting equilibrium conformation of the radical.

For open shells, ab initio LCAO MO SCF calculations were carried out by the unrestricted Hartree–Fock (UHF) method with the 6-31G basis set using the FireFly quantum chemical program package [8], which partially uses the GAMESS code (US) [9]. As a result, groups of spectrally equivalent atomic nuclei composing the HFS simulation scheme were distinguished. The dynamic perturbations were included by adding equations relating spectral parameters (multiple line widths and positions) to reduce the number of variable parameters and to increase the speed and robustness of optimization. The root-mean-square

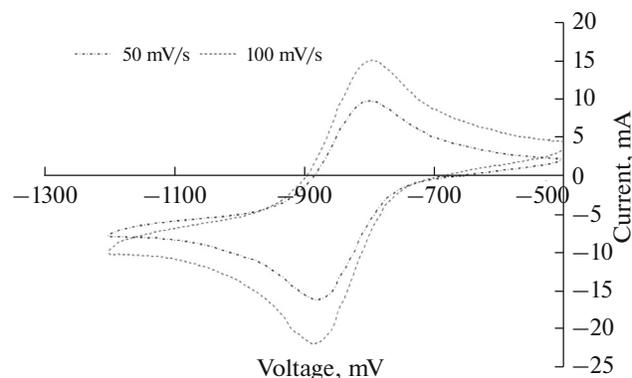


Fig. 2. Cyclic voltammograms of 1-allyl-4,4'-bipyridylium bromide (**3**) in DMF; 0.15 M tetrabutylammonium bromide as the supporting electrolyte, a saturated silver chloride reference electrode; potential sweep rate, mV/s: (1) 5; (2) 10; (3) 20; (4) 50; (5) 100, (6) 150.

deviation of the model data from the experiment served as the target function. The optimization methods included the coordinate descent and conjugate gradients. The calculation results are summarized in Table 2.

The ESR spectra of the radical cations generated from the monosubstituted 4,4'-bipyridylium salts upon electrochemical or photochemical reduction are identical.

According to quantum chemical calculations, the splitting constants α^N , $\alpha^{N'}$, $\alpha_{(2,6)}^H$, $\alpha_{(2,6')}^H$, $\alpha_{(3,5)}^H$, and $\alpha_{(3,5')}^H$ are not equal and the corresponding nitrogen and hydrogen nuclei are non-equivalent. It should be noted that high convergence of the spectra close to 100% was attained using the phenomenological model. The experimental and simulated ESR spectra of the radicals are identical in the form and the number of HFS components; this allows more accurate determination of the pattern of spectral splitting and calculation of HFS constants.

The best resolution was obtained in the ESR spectra of radicals generated by photochemical reduction. Figure 3a shows the high-resolution ESR spectrum of the radical of 1-methyl-4,4'-bipyridylium iodide (**1**) generated by photochemical reduction in 96% ethanol. The pattern of spectral splitting was determined to

Table 1. Cyclic voltammetry characteristics

Compound	E , V	ΔE , mV
1	-0.879 ± 0.008	78
2	-0.950 ± 0.011	72
3	-0.840 ± 0.010	79
4	-0.908 ± 0.008	71
5	-0.826 ± 0.011	77
6	-0.891 ± 0.006	79

Table 2. HFS constants in the ESR spectra of neutral radicals generated from monosubstituted 4,4'-bipyridylium salts by the photochemical process

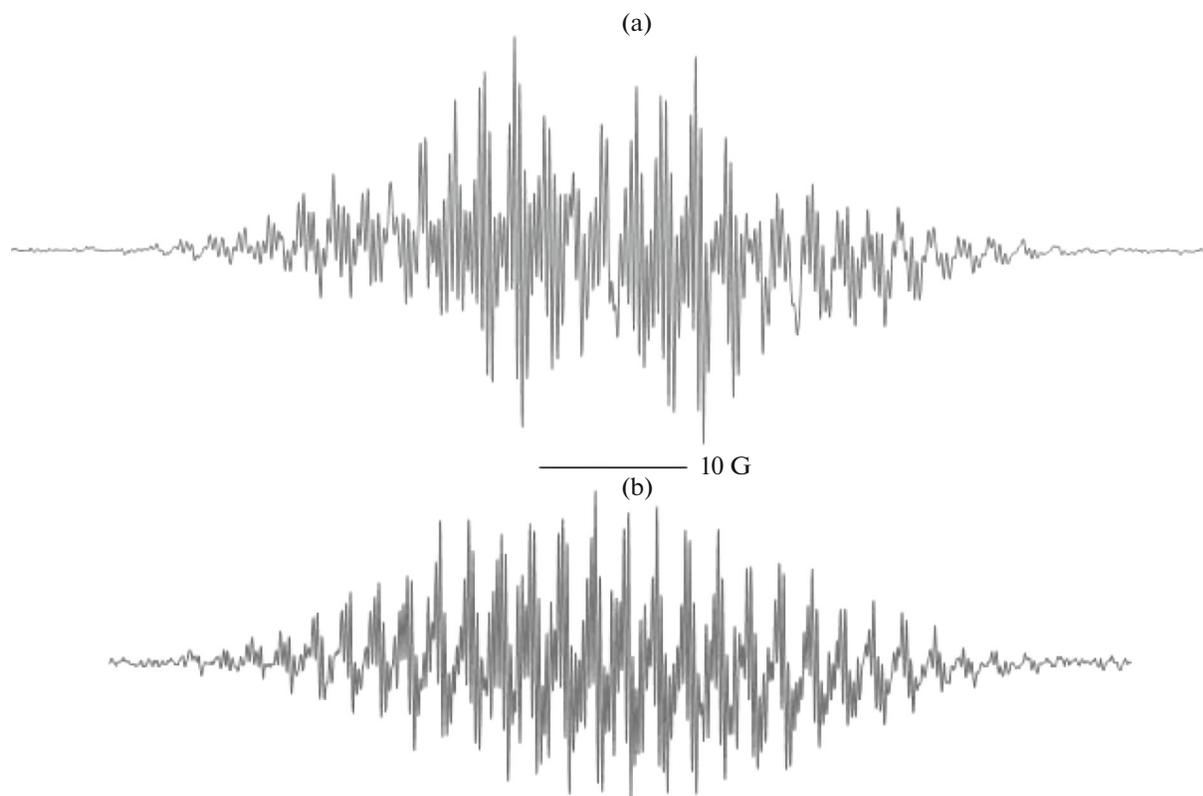
Compound	Splitting constants, G							HFS simulation scheme for the ESR spectrum
	α^N	$\alpha^{N'}$	$\alpha_{(\text{alpha})}^H$	$\alpha_{(2,6)}^H$	$\alpha_{(2',6')}^H$	$\alpha_{(3,5)}^H$	$\alpha_{(3',5')}^H$	
1	6.089	3.940	4.120	1.177	1.650	1.388	1.590	$3N \times 3N' \times 4H(\text{CH}_3) \times 3H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$
2	5.904	3.932	4.080	1.292	1.674	1.477	1.512	$3N \times 3N' \times 4H(\text{CH}_3) \times 3H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$
3	5.336	4.405	2.593	1.276	1.680	1.453	1.529	$3N \times 3N' \times 3H(\text{C}_{\text{alpha}}) \times 3H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$
4	5.501	4.293	2.720	1.339	1.549	1.392	1.429	$3N \times 3N' \times 3H(\text{C}_{\text{alpha}}) \times 3H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$
5	5.323	4.415	2.647	1.245	1.590	1.454	1.574	$3N \times 3N' \times 3H(\text{C}_{\text{alpha}}) \times 3H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$
6	5.551	4.257	2.685	1.370	1.542	1.427	1.442	$3N \times 3N' \times 3H(\text{C}_{\text{alpha}}) \times H(\text{C}_2) \times 3H(\text{C}_2') \times 3H(\text{C}_3) \times 3H(\text{C}_3')$

be $3N \times 3N' \times 4H(\text{CH}_3) \times 3H(\text{C}_{2,6}) \times 3H(\text{C}_{2',6'}) \times 3H(\text{C}_{3,5}) \times 3H(\text{C}_{3',5'})$ and the constants were calculated to be $\alpha^N = 6.089$ G, $\alpha^{N'} = 3.940$ G, $\alpha^H(\text{CH}_3) = 4.120$ G, $\alpha_{(2,6)}^H = 1.177$ G, $\alpha_{(2',6')}^H = 1.650$ G, $\alpha_{(3,5)}^H = 1.388$ G, $\alpha_{(3',5')}^H = 1.590$ G.

Figure 3b shows the high-resolution ESR spectrum of the 1-methyl-4,4'-bipyridylium hexafluorophosphate (**2**) radical cation generated by photochemical reduction in acetonitrile. The pattern of spectral splitting was determined to be $3N \times 3N' \times 4H(\text{CH}_3) \times$

$3H(\text{C}_{2,6}) \times 3H(\text{C}_{2',6'}) \times 3H(\text{C}_{3,5}) \times 3H(\text{C}_{3',5'})$ and the constants were calculated to be: $\alpha^N = 5.904$ G, $\alpha^{N'} = 3.932$ G, $\alpha^H(\text{CH}_3) = 4.080$ G, $\alpha_{(2,6)}^H = 1.292$ G, $\alpha_{(2',6')}^H = 1.674$ G, $\alpha_{(3,5)}^H = 1.477$ G, $\alpha_{(3',5')}^H = 1.512$ G.

Figure 4 shows the ESR spectrum of the 1-allyl-4,4'-bipyridylium bromide (**3**) radical generated by photochemical reduction in 96% ethanol. The spectrum contains about 30 lines instead of 2187 lines. This is attributable to the lack of equivalence of resonating atoms and, hence, different HFS constants, giving rise to overlap and superimposition of spectral lines. The

**Fig. 3.** ESR spectrum of the radical generated from (a) methyl-substituted 4,4'-bipyridylium salt **1** (A = I) in 96% ethanol; (b) **2** (A = PF₆) in acetonitrile.

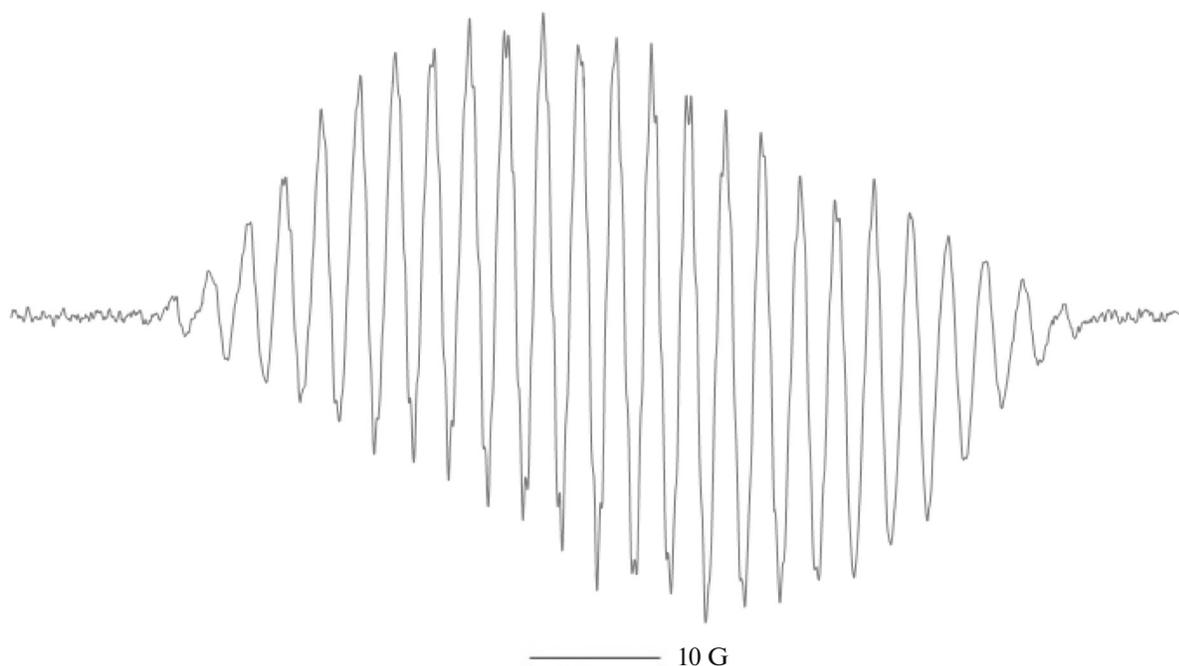


Fig. 4. ESR spectrum of the radical generated from 1-allyl-4,4'-bipyridylium bromide **3** (A = Br) in 96% ethanol.

ESR spectra of compounds **3** and **4** are identical in the form and the number of observable HFS components; the pattern of spectral splitting is also the same: $3N \times 3N' \times 3H(C_{\text{alpha}}) \times 3H(C_{2,6}) \times 3H(C_{2',6'}) \times 3H(C_{3,5}) \times 3H(C_{3',5'})$; however, the corresponding HFS constants are not equal (Table 2). This may be caused by the influence of the type of anion on the electronic structure and by the distribution of the unpaired electron spin density in the molecule.

The ESR spectra of the radicals generated from compounds **5** and **6** possess similar spectral characteristics and similar splitting patterns, but have different HFS constants, like in the case of compounds **3** and **4**.

The influence of the nature of anions of monosubstituted 4,4'-bipyridylium salts on the unpaired electron spin density distribution in the molecule was identified for the first time. The HFS constants we found for compounds **1** (A = I), **3** (A = Br), **5** (A = Cl), **2**, **4**, **6** (A = PF₆) increase in the series **1** (A = I) < **2** (A = PF₆); **3** (A = Br) < **4** (A = PF₆); **5** (A = Cl) < **6** (A = PF₆), or Cl⁻ < Br⁻ < I⁻ < PF₆⁻. The observed trends are caused by the fact that the counter-ion migration slows down as its size increases, which is in good agreement with the conclusion derived from current–voltage characteristics. Also, this can be associated with the electronegativity (on the Pauling scale) of the anion or anion complex and, as a consequence, with the electrostatic interaction strength. One more possible reason is that the aromatic protons are more sensitive to the change in the spin density at lower splitting

constants $\alpha_{(x)}^H$. Therefore, the splitting constants $\alpha_{(2,6)}^H$, $\alpha_{(2',6')}^H$, $\alpha_{(3,5)}^H$, $\alpha_{(3',5')}^H$ are not equal and the corresponding protons are non-equivalent.

A similar situation is encountered in the assignment of the HFS constants in the ESR spectra of the radicals generated from the allyl- (**3** (A = Br), **4** (A = PF₆)) and benzyl-substituted (**5** (A = Cl), **6** (A = PF₆)) 4,4'-bipyridylium salts.

The difference between the HFS constants of methyl-substituted radicals and those of allyl- or benzyl-substituted radicals deserves mention. The rotation of a methyl group is known to be free, resulting in averaged splitting constants. Meanwhile, in the case of allyl or benzyl substituent, one position of the trigonal rotor is occupied by a more bulky group, which serves as a sort of anchor preventing the rotation. The observed splitting is related to the dihedral angle between the π -system and the atomic nucleus in the substituent and is described by the torsion angle function [10], whose special case is the Heller–McConnell equation. The equilibrium orientation of the hydrogen nuclei in allyl and benzyl groups is such that the observed splitting $\alpha_{(\text{alpha})}^H$ is lower than the averaged value observed for the methyl-substituted derivative.

As an example, Fig. 5 shows the kinetic curves for the current passed through the sample vs. time and the curves for transmittance and absorbance vs. time. These results were used to calculate the charge through the sample per unit time

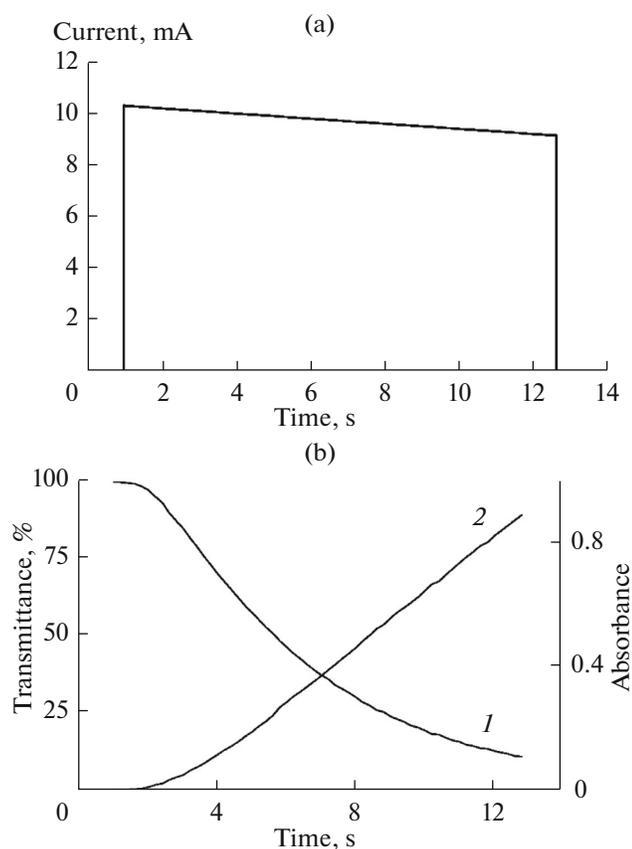


Fig. 5. Kinetic curves of (a) current; (b) (1) transmittance and (2) absorbance during current passage through the sample.

$$q = \int idt,$$

the electrochromic efficiency at the absorption maximum (η_{\max}) for the wavelength λ_{\max} corresponding to the absorption maximum

$$\eta_{\max} = \Delta DS/q = (D - D_0) S / \int idt,$$

and the integral electrochromic efficiency (η_{int})

$$\eta_{\text{int}} = \int (D - D_0) d\lambda S / \int idt,$$

where D and D_0 are the absorbances of the colored and bleached sample; S is the working layer area, cm^2 ; q is the passed charge, C ; i is current, A ; t is time, s .

The integration was done over the current passage time up to coloring intensity of 90% of the maximum value and the integration for absorbance was carried out over the visible wavelength range.

Simultaneously, the transmittance vs. time curves were used to calculate the contrast for coloring at the absorption maximum

$$\Delta T_{\max} = 1 - (I/I_0) \times 100\%,$$

where I and I_0 are the light fluxes having passed through the colored and bleached sample, respectively.

Also the integral transmittance ΔT_{int} was calculated over the whole visible wavelength range ($\int (I/I_0) d\lambda$). The key characteristics of the visible spectra of solutions of monosubstituted salts **1–6** in DMF and their electrochromic characteristics are summarized in Table 3.

The differences between the electrochromic characteristics of the initial bipyridines are related to their chemical structure and predominant formation of neutral radicals in the case of methyl-substituted salt **1** ($A = I$), resulting in a substantially higher absorbance, high contrast, and short switch-on time of the effect. As a consequence, the sample based on *N*-methyl-4,4'-bipyridylium iodide shows a higher electrochromic efficiency than the samples based on allyl- and benzyl-substituted salts. Meanwhile, replacement of the anion does not affect much the electrochromic parameters in the series of compounds **1**, **2**, **3**, **4**, **5**, and **6** and rather decreases the electrochromic efficiency. The passed charge q and the related electrochromic efficiency η also change; the latter value approaches the corresponding value for a solution in DMF.

The results of measurements of the electrochromic characteristics of monosubstituted 4,4'-bipyridylium salts in solutions are in good agreement with the conclusion drawn from quantum chemical calculations and phenomenological simulation of the HFS of the ESR spectra of neutral radicals generated from monosubstituted 4,4'-bipyridylium salts.

Table 3. Electrochromic characteristics

Compound	D_{\max}	τ_{90} , s	λ_{\max} , nm	ΔT_{\max} , %	ΔT_{int} , %	q , mC	η_{\max} , cm^2/C	η_{int} , cm^2/C
1	0.48	13.4	601	92.4	46.6	78.2	132.7	50.5
2	0.48	14.3	605	92.1	46.0	80.9	131.2	50.3
3	0.46	15.6	568	89.0	45.8	89.1	110.4	46.2
4	0.46	16.2	572	89.4	45.1	92.1	108.7	45.8
5	0.39	18.9	564	88.7	39.9	98.4	99.3	41.0
6	0.39	19.8	564	89.2	39.3	102.3	97.5	40.2

τ_{90} is the time required to reach 90% color intensity with respect to the maximum. The concentration of monosubstituted salts in solutions is 0.1 mol/L.

Thus, the following conclusions can be drawn.

(1) The distribution of the unpaired electron density in the radicals generated from monosubstituted 4,4'-bipyridylium salts by two independent methods is virtually identical.

(2) The nature of counter-ions in the radicals generated from monosubstituted 4,4'-bipyridylium salts was found to affect the electrochemical reduction potentials, HFS constants, and electrochromic properties.

(3) A combination of quantum chemical calculations and phenomenological simulation of the HFS for high-resolution ESR spectra was used to determine the precise π -electron density distribution in the radicals generated from monosubstituted 4,4'-bipyridylium salts.

(4) The set of presented methods is suitable for detailed investigation of systems of this type and for their application as the base in photoelectrochromic materials.

ACKNOWLEDGMENTS

This work was supported by the Basic Research Program of the Presidium of the RAS No. 10 "Advancement of Magnetochemical Methods for

Diagnostics of Materials with Paramagnetic Centers" (I.8P3) supervised by Academician Yu.A. Zolotov.

REFERENCES

1. W. R. Boon, *Chem. Ind. (London)*, 782 (1965).
2. H. T. Van Dam and J. J. Ponjee, *J. Electrochem. Soc.* **121**, 1555 (1974).
3. J. F. Willems, *Photogr. Sci. Eng.* **15**, 213 (1971).
4. I. Tabushi and A. Yazaki, *Tetrahedron* **37**, 4185 (1981).
5. T. Kamo and M. Kamura, *Bull. Chem. Soc. Jpn.* **45**, 3309 (1972).
6. L. Roullier and E. Laviron, *Electrochim. Acta* **22**, 669 (1977).
7. *Organic Electrochemistry*, Ed. by M. M. Baizer and H. Lund (Marcel Dekker, New York, 1983; Khimiya, Moscow, 1988).
8. A. A. Granovsky, <http://classic.chem.msu.su/gran/firefly/index.html>.
9. M. W. Schmidt, K. K. Baldrige, J. A. Boatz, et al., *J. Comput. Chem.* **14**, 1347 (1993).
10. E. A. Polenov, *Izv. Akad. Nauk, Ser. Fiz.* **68**, 1066 (2004).

Translated by Z. Svitanko