Reductive cleavage of dichalcogenide bonds
2.* Electrochemistry of bridged bispyridinium systems, electrochemical catalysts of reduction of organic dichalcogenides

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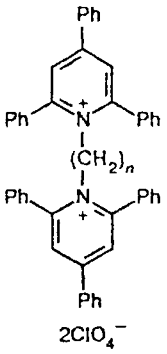
Electrochemical reduction of 1,2-di(2,4,6-triphenylpyridinium-1)ethane, 1,4-di(2,4,6-triphenylpyridinium-1)butane, 1,6-di(2,4,6-triphenylpyridinium-1)hexane, 1,4-di(*N*-methyl-4,6-diphenylpyridinium-2)benzene, and 2,7-di(*N*-methyl-4,6-diphenylpyridinium-2)fluorene in solutions of DMF and MeCN in the potential range from −0.8 to −1.7 V (SCE) was studied by CV. The successive formation of stable radical cations, biradicals, and dianions was investigated by semiempirical MO calculations at the PM3 level.

Key words: bispyridinium, redox catalysis; dichalcogenide bond cleavage; cyclic voltammetry; quantum-chemical analysis, semiempirical methods.

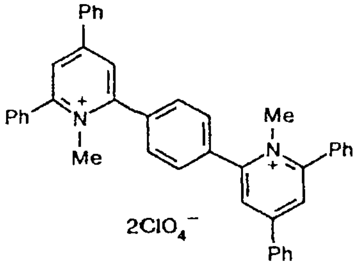
A great body of data on the kinetics and mechanism of electron transfer reactions in biochemical systems, including those using synthetic analogs of biological redox pairs,[2—5] has been accumulated to the present time.

In the final reaction of multistage electron transfer in the synthesis of DNA precursors desoxyribonucleotides, pyridinium carriers induce the cleavage of disulfide groups.[6] Similar reactions of reductive cleavage of disulfide bonds have previously been observed[1] in electrochemical experiments at potentials of the generation of two-electron carriers, biradicals of di(*N*-methyl-4,6-diphenylpyridinium-2)benzene. In this work, we studied the electrochemical properties of dications **1—5**, bearing two equivalent redox centers.**



1—3

n = 2 (**1**), 4 (**2**), 6 (**3**)



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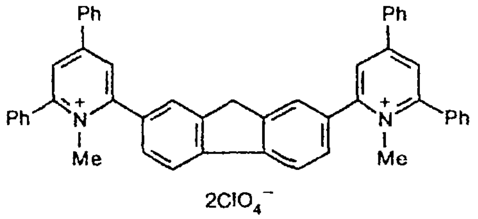
Results and Discussion

Cyclic voltammetry of dications 1—5. The reactivity of several redox centers present in the same molecule depends substantially on the degree of their electron interaction.[7—9] In the majority of cases, multiple non-adjacent electroactive units are electrochemically equivalent.[7,10,11]

According to the character of the voltammetric response, bridged systems **1—5** can produce stable inter-



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* For Part 1, see Ref. 1.

** Mediating properties of dications **1—5** will be published elsewhere.

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mediates. The *three-stage* mechanism, including reversible one-electron stages of the formation of the radical cation and biradical in close potential regions (ΔE_c is 0.09 and 0.130 V in DMF and MeCN, respectively) and two-electron generation of the dianion (E_c ~−1.5 V), characterizes only the reduction of dication **1**, linked by the ethylene chain (Table 1, Fig. 1, *a*). In this case, the energy of interaction between non-adjacent electroactive centers[10,11] is approximated as 1.3—2.2 kcal mol^{-1}.

Formally, the reduction of dications **2** and **3** is characterized by a *two-stage* mechanism. The elongation of the polymethylene chain in these dications converges the first stages, and they are revealed by cyclic voltammetry as one two-electron peak in the potential range from −0.93 to −1.01 V (Fig. 1, *b*). At potential scanning up to −2 V, peaks of reversible formation of dianions **2—5** were detected in the −(1.49—1.59) V potential region (see Table 1).

As a whole, the voltammetric behavior of dications **1—5** is characterized by the appearance of symmetric pairs of cathodic-anodic peaks separated by a value close to the theoretically predicted one (50—60 mV). This indicates a reversible character of the electrochemical reactions studied. The proportionality of the peak height to the square root of the potential sweep (0.05—0.2 V s^{-1}) and also to the content of depolarizer in the system (C_M = 5 · 10^{-4}—5 · 10^{-3} mol L^{-1}) is in agreement with diffusional limitations of the processes studied.[12]

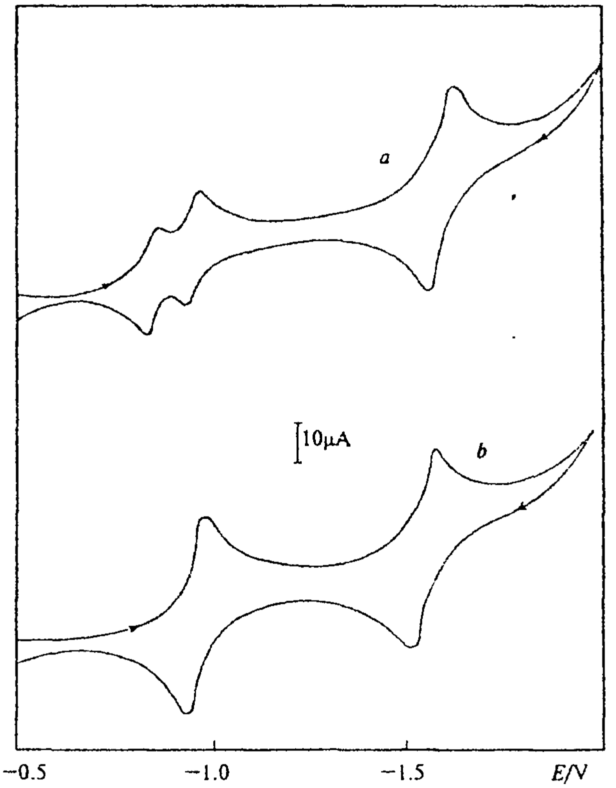

Fig. 1. Cyclic voltammograms of compounds (1 · 10^{-3} mol L^{-1}) **1** (*a*) and **2** (*b*) in MeCN/0.1 *M* Et_4NClO_4 at a Pt electrode (sweep rate 0.1 V s^{-1}).

Table 1. Reduction of compounds **1—5** (10^{-3} mol L^{-1}) in aprotic media at Pt disk electrode by CV (sweep rate 0.1 V s^{-1})

Compound	Solvent	$-E_c$/V	I_c/μA	$-E_a$/V	I_a/μA
1	DMF	0.82	7.5	0.76	7.5
		0.91	7.5	0.85	7.0
		1.47	15	1.42	15
	MeCN	0.82	10	0.76	10
		0.95	10	0.89	10
		1.62	19	1.57	19
2	DMF	0.95	14	0.90	14
		1.50	14	1.45	14
	MeCN	1.00	19	0.95	19
		1.58	19	1.53	19
3	DMF	0.96	14	0.91	14
		1.51	14	1.46	14
	MeCN	1.01	20	0.97	20
		1.59	20	1.54	20
4	DMF	0.97	13	0.92	13
		1.50	13	1.45	13
	MeCN	0.99	19	0.95	19
		1.55	19	1.50	19
5	DMF	1.00	14	0.96	14
		1.49	14	1.45	14
	MeCN	1.03	9[a]	0.99	9*
		1.54	9[a]	1.49	9*

* The salt is poorly soluble; found for a concentration of 5 · 10^{-4} mol L^{-1}.

Quantum-chemical analysis of the stability of electron transfer intermediates of systems 1—5.* The quantum-chemical calculations** performed at the semiempirical PM3 level using the MOPAC program suite[13] confirm that minima on the potential energy surfaces (PES) correspond to systems **1—5**, regardless of charges, and, in all cases, the Hess matrices calculated for them are positively determined.[14] Transition from dications to radical cations and, further, to biradicals in all bispyridinium systems is accompanied by a progressive decrease in the energy. The products of all electrochemical stages are stable (according to the criteria of cyclic voltammetry[12] and results of the quantum-chemical analysis).

Dication **1**$^{2+}$ is most stable in the *anti*-planar conformation **1a** (the dihedral N—C—C—N angle is equal to 180°; heat of formation $\Delta H_f \approx$ 440 kcal mol^{-1}). The energy difference between the most stable conformation and the least stable (*syn*-planar) conformation of **1b** is ~11 kcal mol^{-1}. On going to longer bridged fragments

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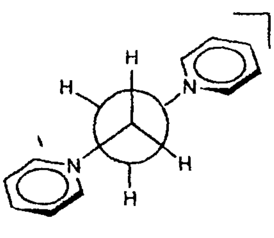
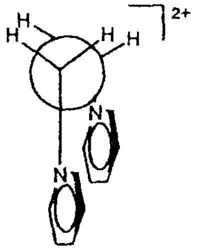
* The results of quantum-chemical calculations will be published in more detail elsewhere.

** The data of gas-phase analysis were confirmed by calculations taking into account the solvation effect.[16]

(dications 2^{2+} and 3^{2+}), the energies of different conformations approach sharply (now the difference in the energy does not exceed 5 kcal mol^{-1}). Any rotations of heterocycles about ordinary C—N bonds are almost independent of each other (the cooperative effect is absent).



1a



1b

A similar situation is observed for radical cations 1—5: according to our calculations, the *anti*-planar and *syn*-planar conformations of **1** are almost isoenergetic. Even in the *syn*-conformation **1b**, any considerable attractive interaction "through space" between the pyridinium rings is absent (the N...N bond order is equal to 0.02). The effect of homoconjugation of the two rings through the methylene bridges is also absent (π-MO of conformer **1b** are mainly localized on the pyridinium rings).

According to the results[15] of calculations at the PM3 level taking into account CI 3×3, like dications and radical cations, biradicals are inherent in minima on PES in the conformations with the rings both closest in space and most remote from one another.

Thus, two-electron transfer mechanisms in the series of bridged systems **1—5** were considered under conditions of the electrochemical experiment in aprotic media (MeCN, DMF). All bispyridinium systems **1—5**, regardless of their structural parameters, undergo stepwise one-electron transformations. In the series of dications 1^{2+}, 2^{2+}, and 3^{2+} taken in their most stable conformations, the energy of the lowest unoccupied MO exhibits a tendency to increase (the energies of LUMO are equal to −8.6, −7.5, and −7.0 eV, respectively). The electrochemical behavior of "isolated" electroactive sites is thus similar to two one-electron reductions of the monocation of *N*-methyl-2,4,6-triphenylpyridinium.[17]

Experimental

IR spectra of samples of compounds **1—5** were recorded in Nujol on a Specord 71-IR spectrometer. Elemental analysis was carried out at the Laboratory of Microanalysis of the Research Institute of Physical and Organic Chemistry (Rostov State University).

2,4,6-Triphenylpyrilium[18] and 1,2,4,6-tetraphenylpyridinium[19] perchlorates and compound **4**[6] were synthesized by the known procedures.

Synthesis of compounds 1—3 (general procedure). 2,4,6-Triphenylpyrilium perchlorate (8 g, 0.02 mol) was dissolved with heating in acetonitrile (20 mL), then the corresponding amine (0.013 mol) was added, and the mixture was boiled for 1 h until the blue luminescence of the solution disappeared. Then acetic acid (5 mL) was added, and the boiling was continued for 20 min. The solution was cooled and diluted with an equal volume of ether. The crystalline product was filtered, washed with ethyl acetate, and dried. After recrystallization from a nitromethane—acetic acid mixture, colorless crystals of salts **1—3** were obtained in 75—85% yield.

1,2-Di(2,4,6-triphenylpyridinium-1)ethane perchlorate (1). Yield 85%, m.p. > 300 °C (decomp.). IR, ν/cm^{-1}: 1620 (C=N); 1580 (C=C); 1100 (Cl=O). Found (%): C, 68.30; H, 4.62; Cl, 8.59; N, 3.20. $C_{48}H_{38}Cl_2N_2O_8$. Calculated (%): C, 68.41; H, 4.52; Cl, 8.44; N, 3.33.

1,4-Di(2,4,6-triphenylpyridinium-1)butane (2) perchlorate. Yield 80%, m.p. > 300 °C (decomp.). IR, ν/cm^{-1}: 1620 (C=N); 1580 (C=C); 1100 (Cl=O). Found (%): C, 69.10; H, 4.68; Cl, 8.30; N, 3.39. $C_{50}H_{42}Cl_2N_2O_8$. Calculated (%): C, 69.04; H, 4.83; Cl, 8.18; N, 3.22. IR, ν/cm^{-1}: 1620 (C=N); 1580 (C=C); 1100 (Cl=O).

1,6-Di(2,4,6-triphenylpyridinium-1)hexane (3) perchlorate. Yield 75%, m.p. > 300 °C (decomp.). IR, ν/cm^{-1}: 1620 (C=N); 1580 (C=C); 1100 (Cl=O). Found (%): C, 69.46; H, 5.03; Cl, 7.99; N, 3.14. $C_{52}H_{46}Cl_2N_2O_8$. Calculated (%): C, 69.57; H, 5.13; Cl, 7.92; N, 3.12.

2,7-Di(*N*-methyl-4,6-diphenylpyridinium-2)fluorene perchlorate (5). Benzalacetophenone (chalcone) (0.02 mol, 4 g) and 2,7-diacetylfluorene (0.01 mol, 2.49 g) were dissolved with heating in acetic acid (40 mL), then a solution (preliminarily prepared in the cold) of perchloric acid in acetic acid (3 mL (0.03 mol) of 70% $HClO_4$ in 9 mL of acetic anhydride) was added, and the mixture was carefully heated to the beginning of boiling, and cooled to −20 °C. The crystals of the bispyridinium salt that formed were filtered off and dissolved in acetonitrile with heating. A 25% aqueous solution of methylamine (3 mL) was added, and the mixture was boiled for 2 h. Acetic acid (10 mL) was added, the mixture was boiled for 1 h, and the product was isolated as described for the synthesis of bispyridinium salts **1—3**. After recrystallization from a nitromethane—acetic acid mixture, the yield of the bispyridinium salt was 2.4 g (28%), m.p. > 300 °C (decomp.). IR, ν/cm^{-1}: 1620 (C=N); 1580 (C=C); 1100 (Cl=O). Found (%): C, 68.99; H, 4.45; Cl, 8.40; N, 3.19. $C_{49}H_{38}Cl_2N_2O_8$. Calculated (%): C, 68.93; H, 4.45; Cl, 8.32; N, 3.28.

The electrochemical experiment has been described in the previous report.[1] Measurements were carried out in a dry argon atmosphere in aprotic media (MeCN, DMF) containing 0.1 *M* tetraethylammonium perchlorate purified by multiple recrystallization from isopropanol (special purity grade), followed by vacuum drying at 80 °C.

A Pt disk electrode with a diameter of 2 mm was used as the working electrode. Potentials were measured relative to the aqueous saturated calomel electrode (SCE) separated from the solution studied in the cell with a bridge filled with a solution of the supporting electrolyte. The potentials were referred to the redox couples ferrocene$^{0/+}$ or decamethylferrocene$^{0/+}$ (E^0 is 0.44 and 0.00 V, SCE, respectively).[20] The number of electrons was determined by comparison of the heights of maximum currents of reduction of the compounds under study with the height of the one-electron peak of reduction of 1,2,4,6-tetraphenylpyridinium.[17]

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