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A Study of Spiro[indoline-pyridobenzopyrans] by Differential Pulse Voltammetry on a Dropping Mercury Electrode and Quantum Chemistry

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Abstract—Spiropyrans of the indoline series were studied by differential pulse voltammetry in DMSO solutions. The experimental data obtained were supported by quantum-chemical calculations performed to examine the structural features and thermodynamic stability of a series of spiro-pyrans. The calculations revealed a correlation between the peak potential (E_p) of spiropyrans and the energy of the lowest unoccupied π orbital. Procedures were developed for identification and quantitative determination of all the spiropyrans in DMSO on a mercury dropping electrode in the concentration range from 1×10^{-7} to 1×10^{-6} M.

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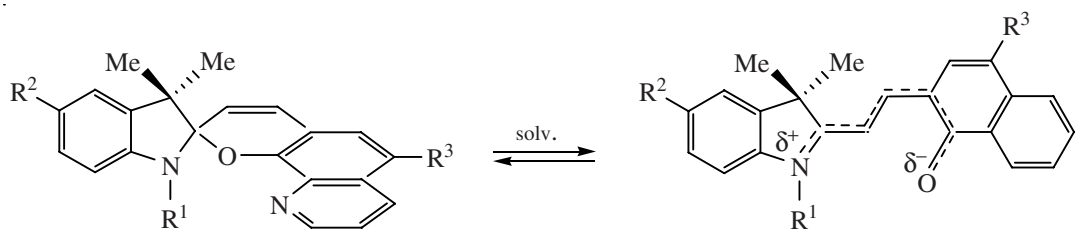
Spiropyrans **A** consist of two heterocyclic fragments, one of which is substituted 2*H*-pyran, sharing a common tetrahedral sp^3-hybridized carbon atom and lying in orthogonal planes.

These systems are used or show promise for photography, analytical chemistry, production of displays, photolithography, textile industry, and liquid flow imaging [1–3], in filters and lenses with variable optical density, including ophthalmologic sun glasses, as optical recording media, etc.

The development of methods for qualitative and quantitative determination of heavy metal ions for medicine and environmental monitoring is an important field of modern sensor research [4]. Spiropyrans are fast photodynamic fluorescent sensors with the possibility of both chemical and photochemical control of the complexation of the merocyanine form with heavy metal ions. As compared to the previously described systems [5, 6], merocyanines are considerably more sensitive and show low fatigue.

One of the most interesting properties of spiropyrans **A** is their transformation into a colored merocyanine-like form **B** by opening of the pyran ring:

Scheme 1.



A **B**

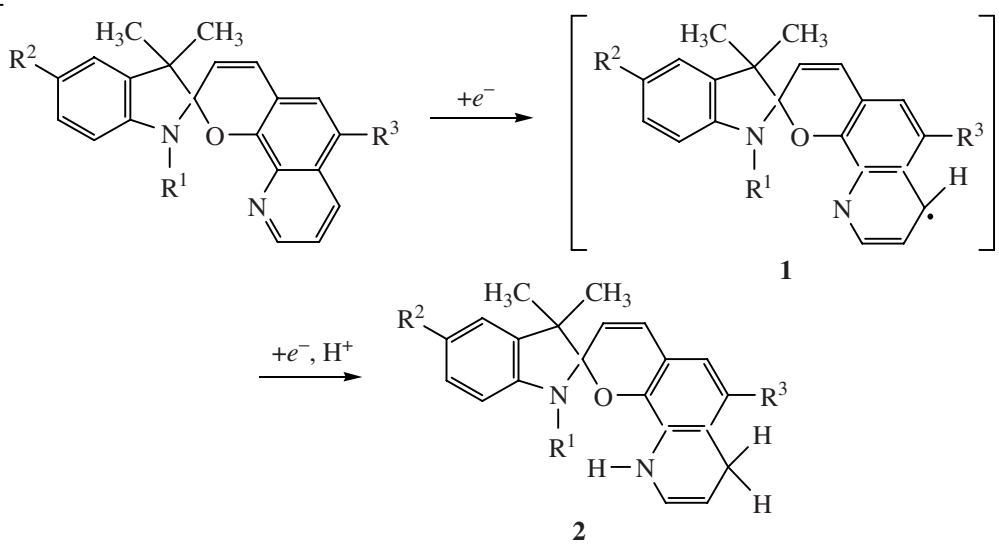
The photochromism of spiropyrans depends on the compound structure (nature of the heteroatom; substituents in different positions of the molecule), medium (solvent, viscosity, etc.), temperature, photolysis energy, and absorption band of the open form.

Here we report on a comprehensive study of certain important spiropyrans. The physicochemical characteristics of spiropyrans were studied by differential pulse voltammetry, and for revealing structure–property relationships we used ab initio and semiempirical methods of quantum chemistry.

As starting compounds we used the following spiropyrans of the indoline series (Scheme 1): **I**, 1,3,3-trimethyl-6'-chlorospiro[indoline-2,2'-[3,2-*h*]pyrido[2*H*-1]benzopyran] (R^1 = CH_3, R^2 = H, R^3 = Cl); **II**, 6'-bromo-1,3,3-trimethylspiro[indoline-2,2'-[3,2-*h*]pyrido[2*H*-1]benzopyran] (R^1 = CH_3, R^2 = H, R^3 = Br); **III**, 1-benzyl-6'-bromo-3,3-dimethylspiro[indoline-2,2'-[3,2-*h*]pyrido[2*H*-1]benzopyran] (R^1 = CH_2Ph, R^2 = H, R^3 = Br); **IV**, 3,3-dimethyl-1-(2-carboxyeth-yl)-6'-chlorospiro[indoline-2,2'-[3,2-h]pyrido[2*H*-1]-benzopyran] (R^1 = CH_2CH_2COOH, R^2 = H, R^3 = Cl); and **V**, 6'-bromo-1,3,3-trimethyl-5-chlorospiro[indoline-2,2'-[3,2-*h*]pyrido[2*H*-1]benzopyran] (R^1 = CH_3, R^2 = Cl, R^3 = Br).

The compounds we studied are crystals readily soluble in polar organic solvents (acetone, DMSO, acetonitrile) and limitedly soluble in nonpolar organic solvents. In DMSO, spiropyrans exist in two forms: **A** and **B**.

Apparently, both forms have active centers and are capable of reduction on a mercury dropping electrode. The initial step of the reduction of spiro form **A** on a mercury dropping electrode is transfer of one electron to the pyridine nitrogen atom of the chromene moiety with the formation of a radical anion.



Radical anion **1** can take up a second electron to form a dianion which in the presence of a proton donor can undergo protonation to dihydro-substituted indoline[pyridobenzopyran] **2**.

We studied the reduction of spiropyrans **I–V** by cathodic differential pulse voltammetry. In the course of reduction of the spiropyrans, we observed two reduction praks corresponding to forms **A** and **B**. The measured reduction peak potentials of spiropyrans **I–V** are given for each form in Table 1.

Reduction of spiropyrans on a mercury dropping electrode. The reduction on a mercury dropping electrode was studies simultaneously for both isomeric forms of spiropyrans **I–V**. For this purpose, we examined the dependence of the limiting current on the square root of the mercury column height $(H_{Hg})^{1/2}$. The mercury column height was measured from the lower cut of the capillary where mercury drops are formed to the horizontal plane of the mercury mirror in the overhead reservoir. In all the cases, the h_p–$(H_{Hg})^{1/2}$ dependences are linear, suggesting the diffuse character of the electrode process (Fig. 1).

Table 1. Reduction peak potentials of spiropyrans **I–V** in DMSO (supporting electrolyte 0.1 M tetrabutylammonium iodide)

Spiropyran	Half-wave potential E_p, V	
	form **B**	form **A**
I	–1.74	–2.05
II	–1.72	–1.95
III	–1.64	–1.91
IV	–1.35	–1.82
V	–1.65	–1.92

We also examined how the rate of feeding the polarizing voltage (mV s^{-1}) affects the peak height (Fig. 2). The optimal rate of feeding the polarizing voltage was 5 mV s^{-1}, because under these conditions the signal had the best shape. To elucidate the character of reduction of spiropyrans **I–V**, we used the procedure for calculating the Semerano test [7]. For all the spiropyrans **I–V**, the Semerano test is in the range 0–0.5. From the calculated Semerano test and from the dependence of the peak height on the square root of the mercury column height in reduction of both forms of spiropyran **II**, we concluded that the reduction is diffusion-controlled with kinetic limitations.

Similar results were obtained for the other spiropyrans **I–V**.

Quantum-chemical calculations. To elucidate the relative stability and ease of cathodic reduction of spiropyrans, we performed quantum-chemical calculations. The composition of LUMO of the closed form of spiropyrans suggests participation of the quinoline fragment of the chromene moiety in the electroreduction. Therefore, one of the voltammetric peaks should be assigned to addition of one electron to the pyridine nitrogen atom of the quinoline moiety with the formation of a radical anion (Fig. 3, form **A**). The LUMO of the open form of spiropyrans is delocalized over the conjugated system between the quinoline and indoline moieties, with the largest contribution corresponding to the bonds between the indoline nitrogen a tom bearing a partial positive charge and the oxygen atom bearing the partial negative charge (Fig. 3, form **B**).

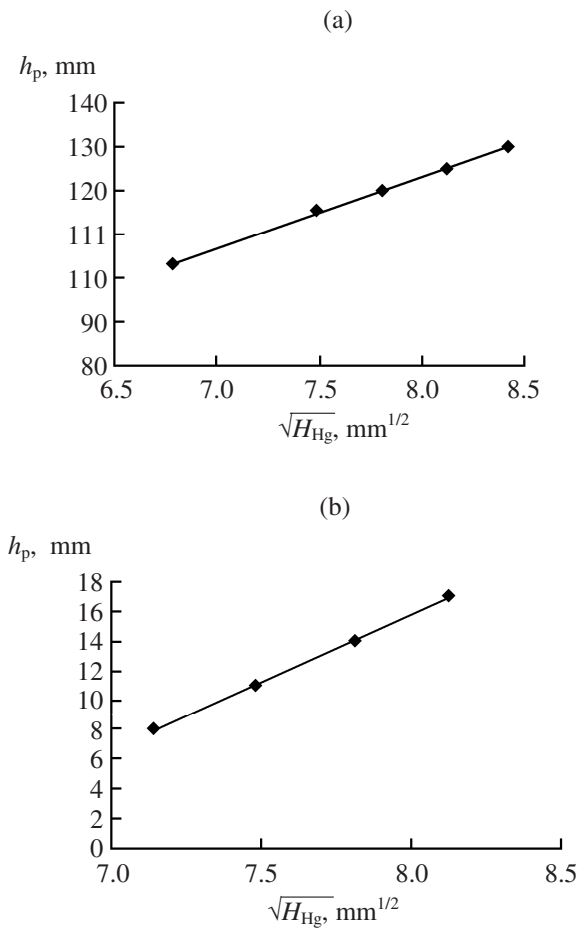


Fig. 1. Peak height as a function of the square root of the mercury column height in reduction of (a) spiro and (b) merocyanine forms of **II**.

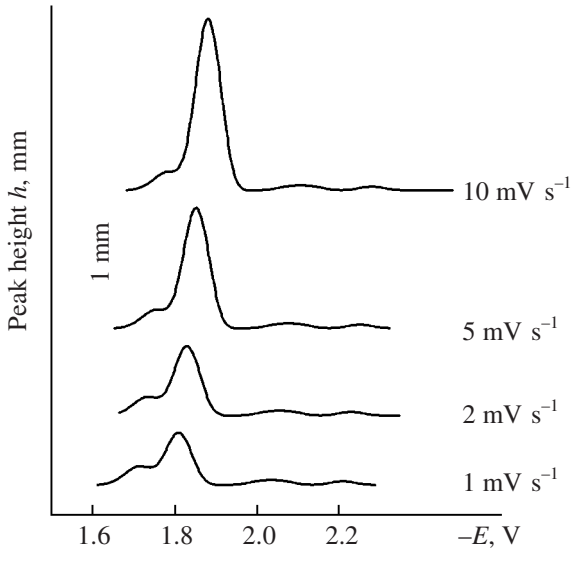


Fig. 2. Peak height and peak potential of the cathodic wave of spiropyran **II** (closed form) at various rates of feeding the polarizing voltage.

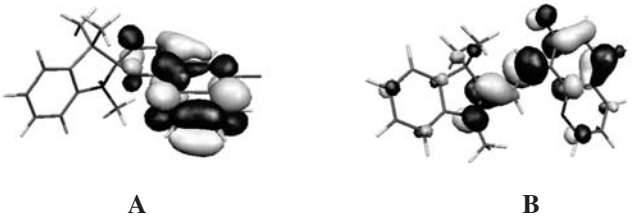


Fig. 3. LUMO of the closed (**A**) and open (**B**) forms of spiropyrans.

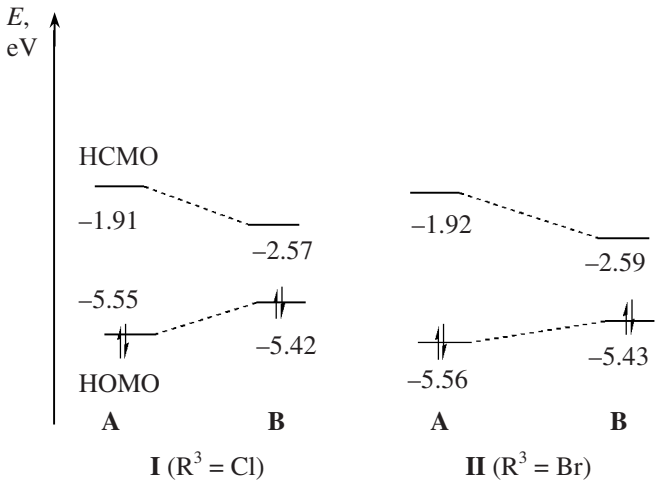


Fig. 4. Comparison of E_{LUMO} of the closed and open forms of spiropyrans **I** and **II**.

This fact suggests that the other reduction peak in the voltammogram corresponds to the electron addition to the merocyanine form with the break of the conjugation chain, followed by the electron delocalization. The values of E_{LUMO} and E_p of spiropyrans reasonably correlate with each other for both forms (Table 2).

Similar results were obtained for the other systems in the series **I–V**. The results of quantum-chemical calculations are obtained with the experimental E_p values in Table 2.

The calculation results unambiguously determine the sequence of reduction of each form of spiropyrans. The lower E_{LUMO} value for the merocyanine form, compared to the spiro form, suggests that specifically this form is reduced first and the electron is taken up relatively readily with the break of the conjugation chain. This fact is confirmed by comparison of the peak potentials E_p, which are considerably higher for the merocyanine form and suggest that the first peak in the voltammogram corresponds to the readily reducible open form and the second peak, to the closed form of spiropyran. Thus, the calculations fully confirmed the experimental data on the higher reducing activity of the merocyanine form (Fig. 4).

The heats of formation of the cyclic (spiro) and open forms of spiro compounds **I–V**, calculated by the PM3 method, are given in Table 3. Similar results were obtained in DFT calculations.

Spiropyrans **I–V** have a somewhat less stable open form. Apparently, this is responsible for the fact that specifically compounds **I–V** are the most inclined to reversible phototransformations.

Plotting the calibration chart. To plot the calibration charts, we prepared a series of solutions with dif-

Table 2. E_{LUMO} and E_p values for spiropyrans in DMSO

Spiropyran	Form **A**		For **B**	
	$-E_p$, V	$-E_{LUMO}$, eV	$-E_p$, V	$-E_{LUMO}$, eV
I	2.05	1.91	1.77	2.57
II	1.95	1.92	1.72	2.59
V	1.92	1.94	1.65	2.63
IV	1.35	1.97	1.82	2.54

Table 3. Heats of formation (kJ mol^{-1}) of forms **A** and **B** of various spiropyrans, according to PM3 calculations

Spiropyran	Open form	Closed form
I	218.97	204.73
II	272.98	262.09
III	387.70	387.70
V	247.86	234.88

Table 4. Results of quantitative determination of spiropyran **I** by differential pulse voltammetry by the reduction peak of the open form in model solutions (n 4, P 0.95)

$c \times 10^7$, M		$s \times 10^9$	s_r
introduced	found		
1.35	1.43	1.6	0.0110
2.11	2.08	1.1	0.0078
6.66	6.72	2.0	0.0030
8.44	8.35	2.2	0.0027

Table 5. Results of quantitative determination of spiropyran **I** by differential pulse voltammetry by the reduction peak of the open form in model solutions (n 4, P 0.95)

$c \times 10^7$, M		$s \times 10^9$	s_r
introduced	found		
1.35	1.39	1.4	0.0101
2.11	2.19	1.7	0.0078
6.66	6.70	2.1	0.0032
8.44	8.41	1.8	0.0021

ferent concentrations of spiropyran in the range from 1×10^{-7} to 1×10^{-6} M. We recorded the voltammograms of the solutions of various concentrations and determined the ranges in which the dependence of the peak current on the concentration is linear. We recorded simultaneously on one voltammogram two peaks corresponding to two forms of spiropyran in solution, which allows quantitative determination of spiropyrans by two peaks simultaneously. Determination by the second peak is more sensitive because of its larger height under the experimental conditions. When plotting the calibration charts, we fulfilled the following conditions: strict constancy of the supporting electrolyte composition (0.1 M tetrabutylammonium iodide), standardization of the temperature and capillary characteristics, and preservation of the constant sensitivity of recording the voltammograms. This allowed the calibration charts to be plotted in the $h = f(c)$ coordinates.

The dependence of the peak height on the concentration of spiropyran **I** in the range from 1×10^{-7} to 1×10^{-6} M is described by the equation $y = 24.7 \times 10^7 c - 10.2$ for the open form (r 0.9945) and $y = 37.1 \times 10^7 c - 6.4$ for the closed form of spiropyran (r 0.9929), where y is the peak height, mm, and c is the concentration of spiropyran **I**, M.

To assess the practical applicability of the suggested method, we treated the results obtained by the introduced–found method for model solutions of spiropyran **I**. The calculation results (Tables 4, 5) show that the method we suggested ensures high repeatbility and correctness of the results and can be used for quantitative determination of the spiropyrans.

We obtained the dependences of the peak height on the concentration of the open and closed forms for all the spiropyrans **I–V**. The dependence of the peak height on the spiropyran concentration is linear in the range from 1×10^{-7} to 4×10^{-6} M for the chosen sensitivity of determination. The quantity s_r for single determination does not exceed 0.0101 for the closed form and 0.0110 for the open form of spiropyrans **I–V**.

EXPERIMENTAL

Measurements were performed with a PA-2 polarograph in the differential pulse mode. Polarization curves were recorded with an XY Recorder-4103 device. A three-electrode temperature-controlled cell was used. The working electrode was a mercury dropping electrode; the reference electrode was a saturated calomel electrode with a potential of +0.247 V; and the auxiliary electrode was a platinum electrode.

Spiro[indoline-pyridobenzopyrans] **I–V** were prepared according to [8]. The working solutions of the compounds were prepared by dissolving the weighed portions in chemically pure grade DMSO. As supporting electrolyte we used a 0.1 M solution of repeatedly recrystallized tetrabutylammonium iodide; the required concentration was determined experimentally.

Prior to each voltammetric run, pure argon was bubbled through the electrolyte for 10 min to remove dissolved oxygen. The electrochemical cell was thermostated at 20°C.

All quantum-chemical calculations were performed with MOPAC program package by PM3 semiempirical method [9] and with TURBOMOLE program package by DFT [10] in the B3LYP and triple-ζ basis sets, using TZVP polarization functions [11]. As the experimental studies were performed in DMSO, the solvent effect was taken into account with COSMO electrostatic model (ε_{DMSO} 46.7) [13].

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