2-Benzoylthioquinazol-4-one (IIIa). To a solution of 1.78 g (0.01 mole) of (I) in 20 ml of DMFA, while stirring, over 15 min we added 1.01 g (0.01 mole) of triethylamine. We then added dropwise 1.41 g (0.01 mole) of benzoyl chloride so that the temperature of the reaction mass did not exceed 20°C. The mixture was stirred for 1 h. The precipitated triethylamine hydrochloride was filtered off, the DMFA was distilled under vacuum, the residue was recrystallized from acetonitrile, and 1.51 g (53%) of (III) was obtained; mp 210-212°C. IR spectrum, cm^{-1}: 1625 (C=N), 1655 (C=O), 1740 (C=O). Mass spectrum, m/z (%): M^+ 282 (7), 254 (9), 253 (8), 178 (20), 132 (7), 122 (16), 105 (100), 77 (67).

Compounds (IIIb-d, IVa-c) were obtained similarly (Table 1).

3-Benzoyl-2-thioxoquinazol-4-one (V). To 50 ml of concentrated sulfuric acid we added 3.0 g (0.01 mole) of 1-(o-carboxyphenyl)-3-benzoylurea in portions. The mixture was left at 20°C for 24 h and was then poured with cooling into 50 ml of a saturated solution of sodium acetate. The precipitate was filtered off, washed with water, and dried in air, and 1.7 g (60%) of compound (V) was obtained; mp 139-140°C (from alcohol). IR spectrum, cm^{-1}: 1630 (C=N), 1658 (C=O), 1735 (C=O). Mass spectrum, m/z (%): M^+ 280 (8), 252 (9), 176 (20), 130 (6), 120 (17), 103 (100), 89 (10), 75 (69).

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ELECTROCHEMICAL OXIDATION OF SUBSTITUTED 1H-1,2-DIAZAPHENALENES

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It was shown by cyclic voltammetry and electrolysis at controlled potential at a platinum electrode and also by TLC and UV spectroscopy that the electrochemical oxidation of substituted 1H-1,2-diazaphenalenes in anhydrous acetonitrile takes place in a single one-electron stage with the formation of a stable radical-cation. The oxidation potentials of a series of derivatives of 1H-1,2-diazaphenalene and the parameters of the equation for the correlation of these potentials with the Taft substituent constants were determined.

1H-1,2-Diazaphenalenes belong to the excess-π peri-heterocyclic compounds. Possessing a high-lying HOMO, the excess-π heterocycles are distinguished by considerable susceptibility to oxidation [1]. Cyclic voltammetry at a standard platinum microelectrode was used for a quantitative assessment of the capacity of compounds of the 1H-1,2-diazaphenalene series for oxidation. The investigated substances are given in Table 1.

As seen from Table 1, at a platinum electrode in acetonitrile solutions compounds (I-X) give one well-defined electrooxidation wave, the half-wave potentials of which lie in the range of 0.5-1.1 V. Figure 1 shows the cyclic current—voltage curve for compound (I), recorded with a potential sweep rate of 1 V/sec. The clear anodic peak and the presence of a cathodic peak comparable with the anodic peak in magnitude show that the oxidation process is reversible. The peak current is limited by the diffusion rate with an insignificant contribution from the adsorption component, as demonstrated by the value of the rate criterion (the slope of the straight line against the logarithm of the peak current and the logarithm of the potential sweep rate), which is equal to 0.60 for the anodic peak and 0.64 for the cathodic peak [2]. The high degree of reversibility in the electrode process is also con-

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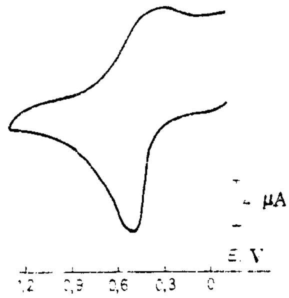


Fig. 1

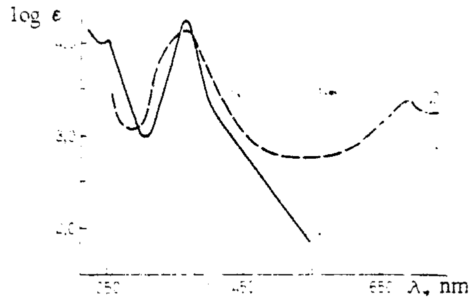
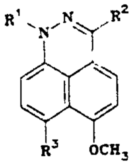


Fig. 2

Fig. 1. Cyclic voltammogram of diazaphenalene (I). Concentration $5 \cdot 10^{-4}$ M.

Fig. 2. Absorption spectra of diazaphenalene (III) (1) and its electrolysis product (2).

TABLE 1. Parameters of the Cyclic Voltammograms for Substituted 1H-1,2-Diazaphenalenes at a Platinum Electrode in Acetonitrile (supporting electrolyte 1 M lithium perchlorate, depolarizer concentration $5 \cdot 10^{-4}$ M)



Compound*	R¹	R²	E_{pa}, V	E_{pk}, V	Compound*	R¹	R²	E_{pa}, V	E_{pk}, V
I	H	CH_3	0.521	0.341	VI	C_6H_5	C_6H_5	0,580	0,524
II	H	C_6H_5	0.538	0,428	VII	CH_3	CH_3	0,752	0,680
III	CH_3	CH_3	0.505	0,404	VIII	C_6H_5	CH_3	0.843	0,710
IV	CH_3	C_6H_5	0.534	0,473	IX	CH_3CO	CH_3	1.043	0,963
V	CH_3	C_6H_5	0.576	0.490	X	CH_3CO	C_2H_5	1,000	0,880

*I-CI, IX, X, R^3 = H; VII, VIII, R^3 = COH.

firmed by the half-width of the peak in the ac polarograms, which for compound (I) is equal to 92 mV. This is close to the theoretical value of 90/n mV for reversible processes [3].

In order to determine the electron transfer rate constants we used the phase-sensitive ac polarographic method [3], which makes it possible to record the capacitance and active components of the alternating current and to calculate the rate constant from their ratio. The value of K_s which we obtained for (III) is 10^{-3} cm/sec, which corresponds to quasi-reversible charge transfer [4]. To determine the number of electrons taking part in the electrochemical reaction we realized prolonged electrolysis for compounds (I) and (III) at a controlled potential of 0.6 V, corresponding to the potential of the diffusion current region. The amount of electricity passing through the solution was determined by means of a copper coulometer in series with the cell and also by numerical integration of the current–time curve. The number of electrons calculated according to Faraday's law was 0.9, which is close to unity.

The electrolysis process was monitored by TLC on Silufol plates with samples from the electrochemical cell. It was found that only one reaction product with $R_f \simeq 0$ (mobile phase chloroform) is formed during electrolysis. The appearance of a band with λ_{max} 685 nm, which fully corresponds to published data [5], in the absorption spectrum (Fig. 2) and the combination of electrochemical parameters show that this product is a stable radical-cation. Its structure was proved by its reduction with zinc dust in absolute acetonitrile to the initial compound (III), which was identified by its UV spectrum, melting point, and R_f value, corresponding to published data [6].

It was not possible to obtain the reduced product from the electrolysis of compound (I) on account, probably, of the lower stability of the radical-cation. This is explained by the possibility of the elimination of a proton from the pyrrole nitrogen atom and subsequent dimerization of the obtained free radical.

Study of the effect of substituents on the oxidation of 1H-1,2-diazaphenalenes showed a correlation between the potentials of the oxidation peaks and the Taft substituent constants taken from [7]. The following correlation equation, calculated by the method of least squares, was obtained:

$$E_{pa}=(0.67\pm0.08)+(0.7\pm0.3)\Sigma\sigma^0\ (r=0.89,\ S=0.1).$$

Unfortunately, the restricted range of substituents did not make it possible to determine the constants of the correlation equation with great accuracy. However, attention must be paid to the large value of the ρ_π constant (0.7), which indicates that the oxidation of 1H-1,2-diazaphenalenes is highly sensitive to the introduced substituents.

EXPERIMENTAL

The current—voltage curves were recorded on a PO-5122 oscillographic polarograph (model 03) and on a PPT-1 ac polarograph. The working electrode was a platinum wire (ℓ = 2.7 mm, d = 0.5 mm), and the auxiliary electrode was a platinum plate with an area of 0.4 cm^2. A saturated silver chloride electrode was used as reference electrode. The supporting electrolyte was lithium perchlorate (1 M) in absolute acetonitrile. Electrochemical oxidation at controlled potential was realized on a P-5848 potentiostat with a platinum electrode having an area of 0.4 cm^2. The initial concentration of the substances amounted to $8\cdot10^{-3}$ M. The UV spectra were recorded on an SF-16 spectrophotometer in a cuvette with a thickness of 1 cm. Thin-layer chromatography was conducted on Silufol UV-254 plates or on an unfixed layer of aluminum oxide with chloroform as mobile phase and iodine vapor as developer.

Reduction of 6-Methoxy-1,3-dimethyl-1H-1,2-diazaphenalenylium Perchlorate. To an acetonitrile solution of the radical-cation, formed after the electrochemical oxidation of 0.036 g ($1.6\cdot10^{-4}$ mole) of compound (III), we added 0.1 g ($1.5\cdot10^{-3}$ mole) of zinc dust. The mixture was stirred for 10 min, and the solution gradually changed from green to yellow. After removal of the acetonitrile the dry precipitate was dissolved in 10 ml of benzene, the inorganic impurities were filtered off, and the solvent was distilled. We obtained 0.029 g (80%) of (III) in the form of yellow crystals; mp 163°C (from benzene).

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