

# SYNTHESIS AND STUDY OF THE SPECTRAL PROPERTIES OF DIQUINONE DERIVATIVES OF HEMATOPORPHYRIN IX

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*Diquinone derivatives of hematoporphyrin IX with different structures of the quinone fragments were synthesized by the method of mixed anhydrides. The compounds obtained were investigated by UV, IR, PMR, and fluorescence spectroscopy. Pronounced quenching of the fluorescence of porphyrin in the porphyrin quinones, which depends on the acceptor properties of the quinones and the spatial orientation of the donor and acceptor, was observed.*

Photosynthesis is one of the most important biological processes. Porphyrin quinone compounds in which the electron acceptors — quinones — are covalently bonded to the photoinduced electron donors — porphyrins — are being used successfully for modeling the primary step in the absorption of light energy and electron transport [1-10].

We have previously synthesized porphyrin quinone compounds on the basis of deuteroporphyrin IX (DP IX) [7, 8, 10]. In continuing these studies we accomplished the synthesis of diquinone derivatives IIIa-f of hematoporphyrin IX dimethyl ether (I) — these diquinone derivatives are new models for the study of the primary electron transfer in photosynthesis. As in the case of diquinone derivatives of DP IX, the covalent bond between the porphyrin and the quinone was realized at the propionic acid residues of the porphyrin.

The length of the covalent chain between the quinone and porphyrin parts is five or seven atoms. A change in the distance between the chromophores makes it possible to determine the dependence of the degree of interaction between the donor and acceptor and the effectiveness of the photoinduced charge separation on the length of the covalent chain. It has been previously shown that the distance between the chromophores affects the effectiveness of the photoinduced charge separation; lengthening the covalent chain increases the lifetime of the charges separated by light, thereby hindering their reverse recombination [5, 6].

The selection of I as the carboxy component was due to the possibility of ascertaining the effect of the methoxyethyl group of I on the spatial organization of the system and the photoinduced transfer of an electron from the porphyrin to the quinone. Compound I has a higher oxidation potential; this constitutes evidence that its electron-donor properties are more effective than the properties of DP IX.

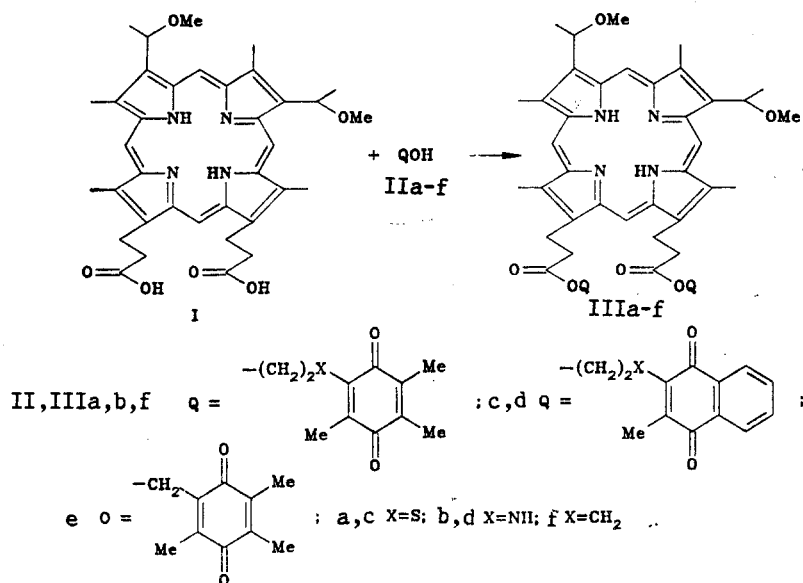
The corresponding quinones IIa-f [7, 10] were used as the hydroxy component. Compound I was obtained by alkaline hydrolysis of tetramethylhematoporphyrin IX (IV) [11].

To create the ester bond we chose the method of mixed anhydrides using di-tert-butyl pyrocarbonate ( $\text{Boc}_2\text{O}$ ) as the activating agent in analogy with the synthesis of diquinone derivatives of DP IX [7], for which this method gave the best results.

The synthesis of diquinone derivatives IIIa-f was carried out in the presence of pyridine and catalytic amounts of 4-dimethylaminopyridine at 0°C. It was shown by TLC that the reaction proceeds considerably more rapidly (by a factor of four to six) than in the case of DP IX and is complete in 15-30 min. After purification by preparative TLC on kieselgel (Merck), the yields of the products ranged from 65.4% to 75.6% (see Table 1). Compound IIIe (33.8% yield) constitutes an exception; this is evidently associated with its lability. According to TLC data, the yield of IIIe in the reaction mixture is 80%, and partial decomposition of the product occurs during chromatographic purification.

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The substance is also unstable during storage and decomposes completely in a month.

The mass spectra confirm the structures of IIIa-f (see Table 2; we observed peaks corresponding, with respect to their  $m/z$  values, to the molecular ion  $M^+$  and to the principal ions formed during fragmentation:  $[M - OCH_3]^+$ ,  $[M - CH(CH_3)OCH_3]^+$ ,  $[M - Q]^+$ , and  $[M - OCOQ]^+$ . In addition, an intense group of signals at 405-460 amu, which is characteristic for the porphyrin ring of this structure and is associated with the elimination of various substituents of the porphyrin ring during mass spectrometry, is present in the spectra of porphyrin quinones IIIa-f.

The IR spectra of IIIa-f are in complete agreement with their structure (Table 1). Bands of stretching vibrations of quinone double bonds were not observed for IIIe, f, evidently because they are hidden under the very intense band of stretching vibrations of the quinone carbonyl group.

The electronic spectra of all of the diquinone derivatives IIIa-f do not differ from the spectrum of IV and are the superimposition of the spectra of the porphyrin and quinone parts (Table 1). This indicates the absence of an interaction between the chromophores in the ground state [1-3].

In addition to confirming the structure of the synthesized IIIa-f (see Table 3), the PMR spectra make it possible to draw a preliminary conclusion regarding the spatial orientation of the porphyrin and quinone fragments of the molecule. The location of the signals of the protons of the porphyrin ring of IIIa-f remain virtually unchanged as compared with the location of the signals of IV ( $\Delta\delta = 0.01-0.8$  ppm), while the signals of the protons of the quinone residue in IIIa-f are shifted to the strong-field region as compared with the signals of the starting quinones. This is associated with the effect of the magnetic anisotropy of the porphyrin ring and constitutes evidence that the quinone part approaches the porphyrin plane [3]. In the case of IIIc, d the signals of the aromatic protons of the quinone residues are shifted 0.28-0.80 ppm to the strong-field region, while the singlet of the methyl group of the quinone is shifted 0.48-0.88 ppm. In the spectra of IIIc, d the signal of the methyl group of the quinone is resolved in the form of two singlets (3H each), which indicates the nonequivalence of the quinone substituents in the 6 and 7 positions of the porphyrin. The signals of the protons of the methyl groups for IIIb, f are represented in the form of six singlets, as compared with four singlets for IIIe and three singlets for IIIa. In the case of IIIa, b, e, f the signals of the methyl groups of the quinone residues are shifted 0.24-0.96 ppm to strong field. For IIIb two of these signals, related to the methyl groups in the 5 and 6 positions of the quinone, are resolved in the form of a quartet ( $J = 1.2$  Hz); this is probably due to the existence of a long-range interaction through the double bond between the methyl groups of the quinone part.

The signal of the proton of the NH group of the quinone for IIIb, d is also shifted 0.67-1.01 ppm to strong field, resolving itself in the form of two triplets; this is due to the nonequivalence of the quinone substituents in the 6 and 7 positions of the porphyrin.

For compounds that contain a nitrogen atom in the covalent chain the signals of the NH group of the quinone, the methyl groups of the quinone for IIIId, and the methyl groups in the 3 and 5 positions of the quinone for IIIb have the greatest  $\Delta\delta$  values; this is associated with their greatest proximity to the porphyrin plane.

TABLE 1. Characteristics of Porphyrin Quinones IIIa-f

Com- pound	$R_f$ (system)	Electronic spectrum (chloroform), $\lambda_{max}$ , nm (log $\epsilon$ )	IR spectrum (in mineral oil or KBr), $\nu$ , $cm^{-1}$				$fI \cdot 10^{-3}$ , rel. units*	Yield, %
			NH	ester CO	quin- one CO	quin- one C=C		
IIIa	0,48 (1)	623,3 (3,73), 570,1 (3,90), 534,5 (4,04)	3280	1720	1625	1575	22,7	75,6
	0,42 (4)	499,9 (4,26), 402,1 (5,34)						
IIIb	0,48 (1)	622,9 (3,65), 569,7 (3,87), 533,3 (4,04)	3280	1720	1650	1580	208	71,5
	0,35 (4)	500,1 (4,24), 402,1 (5,26)						
IIIc	0,52 (1)	623,5 (3,52), 569,9 (3,72), 534,1 (3,90)	3270	1720	1649	1580, 1550	87	65,4
	0,76 (3)	499,9 (4,11), 402,3 (5,25)						
III d	0,56 (2)	621,5 (3,62), 568,9 (3,78), 535,3 (3,92)	3270	1720	1670	1585, 1560	312	71,7
	0,51 (3)	498,9 (4,06), 402,3 (5,18)						
IIIe	0,41 (1)	622,7 (3,53), 568,5 (3,73), 534,3 (3,85)	3270	1720	1630	—	65,4	33,8
	0,40 (3)	499,9 (4,06), 402,1 (5,16)						
III f	0,50 (1)	623,7 (3,55), 569,9 (3,71), 534,3 (3,86)	3270	1718	1624	—	80	73,7
	0,73 (3)	499,7 (4,07), 402,1 (5,19)						

\* $\lambda_{fl}$  620 nm;  $\lambda_{exc}$  400 nm;  $c = 10^{-5}$  mole/liter.

TABLE 2. Mass Spectra of Porphyrin Quinone Derivatives IIIa-f

Com- pound	Fragmentation, m/z, amu ( $I_{rel}$ , %)				
	$M^+$	$[M - OCH_3]^+$	$[M - CH(CH_3) \cdot OCH_3]^+$	$[M - Q]^+$	$[M - QOCO]^+$
IIIa	1042,9 (100)	1011,1 (66,1)	—	831,3 (22)	788,3 (24)
IIIb	1009,1 (100)	—	—	816,9 (32)	773,4 (34)
IIIb*	1087,5 (100)	1056 (32)	1030 (8)	—	812,7 (16)
IIIc	1053,9 (100)	1022,5 (11)	—	—	795,3 (10)
III d**	951,8 (4)	920 (2)	—	788,4 (35)	—
IIIe	1007,1 (100)	975,9 (21)	949,6 (8)	—	771,8 (12)

\*Also detected was a peak with m/z 1072 (16), which corresponds to the  $[M - CH_3]^+$  ion.

\*\*Also detected was a peak with m/z 889,8 (20), which corresponds to the  $[M - 2OCH_3]^+$  ion.

Sulfur atoms change the spatial orientation of the quinones relative to the porphyrin; this is reflected in a change in the PMR spectrum. One observes an overall decrease in  $\Delta\delta$  that is associated with removal of the quinone parts from the porphyrin plane as compared with IIIb, d; all three methyl groups for IIIa (their  $\Delta\delta$  values are approximately identical) and the methyl group and the aromatic protons of the quinone for IIIc have the greatest shifts. This is evidently associated with the fact that angle of inclination of the plane of the quinone rings to the porphyrin plane for sulfur-containing IIIa, c is considerably smaller than for nitrogen-containing IIIb, d.

In the case of derivative IIIf, which does not contain a heteroatom in the covalent chain, one of the methyl groups of the quinone and the  $\alpha$ -CH<sub>2</sub> group of the covalent chain are closest to the porphyrin plane; this leads to the greatest shift of the signals of the protons from these groups.

In comparing the benzoquinone and naphthoquinone structures of derivatives IIIa-d one should emphasize that naphthoquinone derivatives IIIc, d have greater  $\Delta\delta$  values than benzoquinone derivatives IIIa, b.

A comparison of the PMR spectra of derivatives IIIa-f and the analogs based on DP IX [7, 10] shows that the  $\Delta\delta$  values of the protons of the quinone part of derivatives IIIa-f are smaller than the  $\Delta\delta$  values of the derivatives of DP IX. This is evidently due to the steric hindrance during the approach of the quinones to the porphyrin ring that arises in connection with the presence of methoxyethyl groups in the 2 and 4 positions of the porphyrin.

TABLE 3. PMR Spectra of Porphyrin Quinones IIIa-f and IV

Com- pound	Chemical shift (deuteriochloroform), $\delta$ , ppm (SSCC, J, Hz)											
	Quinone CH <sub>arom</sub> (m)	Quinone CH <sub>s</sub> (s)	NHCH <sub>3</sub> (broad t, 3H)	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O NHCH <sub>2</sub> CH <sub>2</sub> O SCH <sub>2</sub> CH <sub>2</sub> O	CH <sub>2</sub> O (t)	meso -H (s 1H)	CH <sub>3</sub> porphyrin (s 3H)	CH <sub>2</sub> CH <sub>2</sub> CO (t, 4H)	CH <sub>2</sub> CH <sub>2</sub> CO (t, 2H)	CH <sub>2</sub> CH (q)	CH <sub>2</sub> CH (d, 3H)	OCH <sub>3</sub> (s, 6H)
IV*	—	—	—	—	—	10.55; 10.51; 10.10; 10.05	3.71; 3.70; 3.62; 3.61	4.40 (J=7.3)	3.29 (4H, J=7.3)	6.05 (2H, J=6.6)	2.26, 2.25 (J=6.6)	3.63
IIIa	—	1.90 (6H); 1.80 (6H); 1.72 (6H)	—	3.09 (4H, t, J=6.1)	4.20 (4H, J=6.1)	10.55; 10.50; 10.10; 10.06	3.71 (6H); 3.61 (6H)	4.45 (J=7.0)	3.30 (4H, J=7.0)	6.08 (2H, J=6.6)	2.28 (6H, J=6.6)	3.65
III b	—	1.70 (q, 3H); 1.66 (q, 3H, J=1.2); 1.51 (3H); 1.48 (3H); 1.49 (q, 3H); 1.41 (q, J=1.2)	4.99, 4.93 (J=6.0)	3.27 (q, 2H); 3.22 (q, 2H, J=6.0)	4.12 (2H); 4.09 (2H); J=6.0	10.54; 10.48; 10.10; 10.09	3.70 (6H); 3.63 (6H)	4.44 (J=7.3)	3.54, 3.36 (J=7.3)	6.05 (2H, J=6.6)	2.27, 2.26 (J=6.6)	3.66
IIIc	7.78...7.67 (4H); 7.37...7.29 (4H)	1.96 (3H); 1.64 (3H)	—	3.21 (t, 2H); 3.08 (t, 2H, J=6.0)	4.26 (2H); 4.23 (2H); J=6.0	10.51; 10.48; 9.98; 9.97	3.70; 3.66; 3.61; 3.58	4.36 (2H); 4.35 (2H); J=6.9	3.23, 3.18 (J=6.9)	6.06 (1H); 6.05 (1H, J=6.6)	2.28, 2.27 (J=6.6)	3.64 (3H); 3.62 (3H)
IIId	7.75...7.63 (2H); 7.50...7.36 (2H); 7.31...7.17 (4H)	1.52 (3H); 1.26 (3H)	5.16, 4.98 (J=5.8)	3.23 (q, 2H); 3.11 (q, 2H, J=5.1)	4.12 (2H); 4.09 (2H); J=5.1	10.45; 10.40; 10.10; 9.97	3.66; 3.65; 3.62; 3.61	4.45 (J=6.9)	3.40, 3.38 (J=6.9)	6.03 (1H); 6.02 (1H, J=6.6)	2.27, 2.26 (J=6.6)	3.63
IIIe	—	1.55 (6H); 1.40 (3H); 1.38 (3H); 1.25 (6H)	—	—	3.70 (s, 4H)	10.55; 10.50; 10.40; 10.22	3.60 (12H)	4.41 (J=6.9)	3.29 (4H, J=6.9)	6.06 (2H, J=6.6)	2.25 (6H, J=6.6)	3.62
IIIe**	—	1.71 (3H); 1.70 (3H); 1.61 (3H); 1.57 (3H); 1.21 (3H); 1.06 (3H)	—	1.25 (4H, t, J=7.5)	3.94 (2H); 3.93 (2H); J=6.0	10.46 (2H); 10.10; 10.08	3.70; 3.69; 3.63 (6H)	4.46 (J=7.0)	3.32, 3.31 (J=7.0)	6.04 (2H, J=6.6)	2.27, 2.26 (J=6.6)	3.66

\*A signal is present at 3.66 ppm (6H, s, COOCH<sub>3</sub>).\*\*A signal is present at 1.38 ppm (4H, t, J<sub>1</sub> = 6.0 Hz, J<sub>2</sub> = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).

As a result of measuring the fluorescence spectra of IIIa-f we established that their fluorescence intensities are much lower than in the case of the starting porphyrin I. The quenching of the fluorescence is evidently associated with intramolecular electron transfer from the porphyrin fragment to the quinone acceptor [1-6, 9, 10]. Thus the quenching of the fluorescence of the porphyrin decreases in the order IIIa > IIIe > IIIf > IIIc > IIIb > IIIId and, with respect to the intensity of the fluorescence of IV in acetone, amounts to a factor of 44, 15.3, 12.5, 11.5, 4.8, and 3.2, respectively; the electron-acceptor activity of the quinone substituents, which is characterized by the polarographic potentials of the half-waves of the reduction of the starting quinones, decreases in the order IIIa > IIIc > IIIf > IIIb > IIIId [12]. Thus the data obtained in measuring the effectiveness of the quenching of the fluorescence of derivatives IIIa-f correlate with the electron-acceptor activities of the quinone substituents. The more pronounced quenching of the fluorescence in the case of IIIf can be explained by the fact that not only the energy parameters but also the spatial orientation of the donor and acceptor affect the effectiveness of intramolecular charge separation, since, according to the PMR data, the quinone substituents in IIIf, which does not contain a heteroatom, are located considerably closer to the porphyrin plane than in sulfur-containing IIIa, c.

## EXPERIMENTAL

The condensations were carried out in anhydrous solvents. The individuality of the compounds and the progress of the reactions were monitored by TLC in the following systems: Silufol UV-254, chloroform—methanol (30:1) (1), chloroform—methanol (15:1) (2); Merck F-254 kieselgel, chloroform—methanol (30:1) (3), chloroform (4). The IR spectra were recorded with a Shimadzu IR-435 spectrometer. The electronic spectra were obtained with Shimadzu UV-240 and SF-18 spectrophotometers. The fluorescence spectra were recorded with a Shimadzu RF-540 spectrofluorimeter. The PMR spectra of solutions in  $\text{CDCl}_3$  were recorded with a Bruker MSL-200 spectrometer (200 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectra were recorded with an MSBK time-of-flight mass spectrometer (Sumy, "Elektron" Planning Department) with ionization by the fission products of californium-252; the sample were applied to nitrocellulose in the form of solutions in chloroform.

The results of elementary analysis for C, H, and N for I and IV were in agreement with the calculated values.

**2,7,12,18-Tetramethyl-3,8-bis(1-methoxyethyl)-13,17-bis(2-methoxycarbonyl)ethylporphyrin (IV,  $\text{C}_{38}\text{H}_{46}\text{N}_4\text{O}_6$ ).** A 5-g (7.7 mmole) sample of protohemin IX was maintained for 3 days in 50 ml of glacial acetic acid saturated with HBr (d 1.45), after which the solvent was removed in vacuo, and the residue was dissolved in 100 ml of methanol. The methanol solution was stirred for 12 h at 20°C, and 150 ml of water and 100 ml of saturated sodium acetate solution were added to the reaction mixture. The resulting precipitate was removed by filtration and chromatographed with a column (5 by 40 cm) packed with activity III (neutral)  $\text{Al}_2\text{O}_3$  by elution with chloroform to give 4.6 g (92%) of IV. Electronic spectrum (in chloroform),  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 623 (3.59), 569 (3.77), 534 (3.91), 500 (4.11), 401 nm (5.22) (Soret).

**B.** A 5-g (7.7 mmole) sample of protohemin IX was maintained for 4 days in 35 ml of glacial acetic acid saturated with HBr, after which the reaction mixture was poured into 600 ml of methanol. After 12 h, 200 ml of a saturated aqueous solution of sodium acetate was added, and the mixture was allowed to stand for 12 h. The precipitated crystals were removed by filtration and washed with hot water and aqueous alcohol to give 4.6 g (92%) of IV, which was identical to the compound obtained by method A.

**2,7,12,18-Tetramethyl-3,8-bis(1-methoxyethyl)-13,17-bis(2-carboxyethyl)porphyrin (I,  $\text{C}_{36}\text{H}_{42}\text{N}_4\text{O}_6$ ).** A 1-g (1.53 mmole) sample of IV was dissolved in 20 ml of dioxane, the solution was heated to 70°C, and a solution of 200 mg (5 mmole) of NaOH in 3 ml of water was added to the hot solution. The reaction mixture was then stirred for 1 h at 70°C until starting IV had disappeared completely, after which 150 ml of water and 1 ml of acetic acid were added. The resulting precipitate was removed by filtration, washed thoroughly with hot water, and dried in a vacuum desiccator over phosphorus pentoxide. Electronic spectrum (in chloroform),  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 623 (3.56), 570 (3.75), 533 (3.89), 500 (4.09), 400 nm (5.22) (Soret). The yield was 0.9 g (94%).

**General Method for Obtaining Diquinone Derivatives IIIa-f.** A 100-mg (0.16 mmole) sample of porphyrin I was dissolved in a mixture of 3 ml of pyridine and 20 ml of dry chloroform, 0.64 mmole of the corresponding quinone IIa-f was added, the mixture was cooled to 0°C, and 148 mg (0.64 mmole) of  $\text{Boc}_2\text{O}$  was added. After 10 min, 5 mg (0.04 mmole) of 4-dimethylaminopyridine was added, and the mixture was stirred for 30 min at 20°C. It was then poured into 300 ml of 2% hydrochloric acid, and the acidic mixture was extracted with chloroform (50 ml). The extract was washed with water (3 × 200 ml) and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed in vacuo, and the residue was separated preparatively on plates (25 by 25 cm) on kieselgel 0.08 mm (Merck) by elution with chloroform—hexane (1:1, 2:1, 4:1). The principal porphyrin band was separated, the solvent was removed, and the residue was triturated in pentane and dried over phosphorus pentoxide and paraffin in vacuo.

## LITERATURE CITED

1. T.-F. Ho, A. R. McIntosh, and A. C. Weedon, *Can. J. Chem.*, **62**, 967 (1984).
2. J. L. Y. Kong and P. A. Loach, *J. Heterocycl. Chem.*, **17**, 737 (1980).
3. S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, M. Migita, T. Okada, and N. Mataga, *Tetrahedron Lett.*, **22**, 2099 (1981).
4. J. R. Bolton, T.-F. Ho, S. Liauw, A. Siemiarzuk, C. S. K. Wan, and A. C. Weedon, *J. Chem. Soc., Chem. Commun.*, No. 9, 599 (1985).
5. D. Gust and T. Moore, *J. Photochem.*, **29**, 173 (1985).
6. M. Migita, T. Okada, N. Mataga, S. Nishitani, N. Kurata, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **84**, 263 (1981).
7. V. V. Borovkov, E. I. Filippovich, and R. P. Evstigneeva, *Khim. Geterotsikl. Soedin.*, No. 5, 608 (1988).
8. R. P. Evstigneeva, V. V. Borovkov, E. I. Filippovich, and S. I. Sviridov, *Dokl. Akad. Nauk SSSR*, **293**, 1130 (1987).
9. V. V. Borovkov, R. P. Evstigneeva, L. N. Strekova, E. I. Filippovich, and R. F. Khairutdinov, *Usp. Khim.*, **58**, 1032 (1989).
10. V. V. Borovkov and R. P. Evstigneeva, Conference Proceedings FECS of the 5th International Conference on the Chemistry and Biotechnology of Biologically Active Natural Products, Varna, Bulgaria, Vol. 3 (1989), p. 412.
11. G. V. Kirillova, G. V. Ponomarev, V. G. Yashchunskii, and T. A. Babushkina, USSR Author's Certificate No. 857,138; *Byull. Izobret.*, No. 31, 115 (1981).
12. V. V. Borovkov, Master's Dissertation, Moscow Institute of Fine Chemical Technology, Moscow (1988).

### EFFECT OF THE pH OF THE MEDIUM ON THE ELECTRONIC ABSORPTION SPECTRA AND STRUCTURE OF 3-METHYL-1-PHENYL-4-PHENYLAZO-5-PYRAZOLONE

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*On the basis of the electronic absorption spectra it was found that 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone exists in acidic solutions in mono- and diprotonated forms. It was established by means of calculations by the Pariser—Parr—Pople (PPP) method that in the neutral and protonated forms the quinone hydrazone tautomer of the phenylazopyrazolone is more stable than the azo tautomer, and it was determined that the protonation center is the  $N_{(2)}$  atom of the pyrazolone ring. The diprotonated form is most likely the quinone hydrazone tautomer protonated at the heteroring  $N_{(2)}$  atom and the  $\alpha$ -nitrogen atom of the azo group. In an alkaline medium the phenylazopyrazolone exists in the form of an anion with predominance of the azo form. The effect of substituents on the diazo component of the phenylazopyrazolone on the long-wave bands of the electronic absorption spectra in various media was explained on the basis of calculation of the distribution of the  $\pi$ -electron density during electron transitions.*

3-Methyl-1-phenyl-4-phenylazo-5-pyrazolone (PAP) and its derivatives are used in the textile industry as dyes for fibers and plastics [1]. The results of a study of the structures and properties of these compounds were correlated in [2, 3]. It was found that PAP exists in the form of a quinohydrazone (QH) tautomer in neutral solutions and in the crystalline state [2, 4, 5]. The hydrazone structure of PAP was proved by IR spectroscopy [6], NMR spectroscopy [7], and x-ray diffraction analysis [8]. On the basis of the electronic absorption spectra (EAS) it was concluded that in alkaline media PAP exists in the form of an anion of the azo-OH form (A) [9-11]; the Raman spectroscopic data also indicate an azo enol structure of the PAP anion [12]. At the same time, the EAS and

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