

The diethyl ester of mesoporphyrin IX and its complex with Pd(II) served as sensitizers for the formation of 1O_2 ; the sensitizer concentration was $5 \cdot 10^{-6}$ mole-liter $^{-1}$.

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CALCULATION OF THE ELECTRONIC STRUCTURE AND DIPOLE MOMENTS OF 4-SUBSTITUTED TETRABROMOPYRIDINES

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It is demonstrated from the results of a quantum-chemical calculation by the CNDO/2 (complete neglect of differential overlap/2) method and the experimental dipole moments for a number of 4-substituted tetrabromopyridines that the character of the intramolecular interactions in the investigated compounds differs little from that observed for 4-substituted nonhalogenated pyridines. A linear relationship between the charge on the heteroatom and the σ_p constants for the substituents in the 4 position was observed. A similar relationship was obtained for the experimental dipole moments and the substituent constants.

In the present research we examined a number of 4-substituted tetrabromopyridines, for which we made a calculation of the electronic structure by means of the standard CNDO/2 (complete neglect of differential overlap/2) program [1] in order to study the distribution of the electron density and the transmission of the electronic effects in the investigated molecules. Similar data were previously obtained within the CNDO/2 approximation for fluorine- and chlorine-containing pyridines [2].

The geometrical parameters for the calculation were selected from the fragments of similar molecules [3-6]. The pentabromopyridine molecule was assumed to be planar. Since

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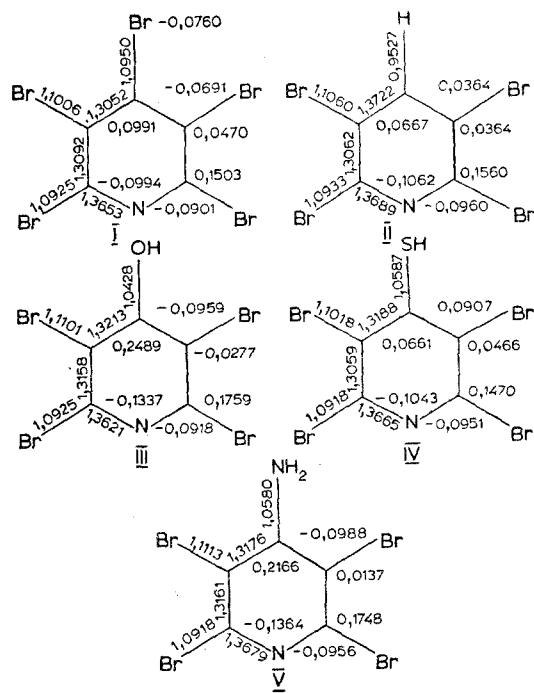


Fig. 1. Distribution of the electron density on the atoms and in the bonds in 4-substituted tetrabromopyridines. The calculated dipole moments are: I) 0.6985; II) 2.3718; III) 2.4950; IV) 1.1096; V) 3.1201 D.

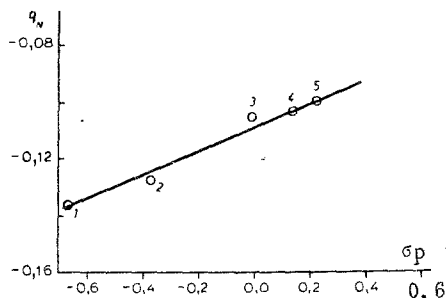


Fig. 2. Dependence of the charge on the nitrogen atom on the constants of substituents in the 4 position: 1) NH₂; 2) OH; 3) H; 4) SH; 5) Br.

the dipole moments are conveyed satisfactorily within the framework of the method used, the experimental dipole moments were obtained for the investigated molecules by means of the second Debye method.

The molecular diagrams of the examined compounds are presented in Fig. 1. Two variants of the orientation of the substituents, viz., a variant with the hydrogen atom in the plane of the pyridine ring and a variant with the hydrogen atom in a plane perpendicular to the ring, were calculated for the III and IV molecules. In the first case the overall energy of the molecules proved to be lower, and the difference in the energies was ~ 7 kcal/mole. This value is of the same order as the energy of the formation of hydrogen bonds, and the energetic advantageousness of this conformation may be due to the formation of an intramolecular hydrogen bond with the bromine atom, as well as to the more favorable orientation of the orbitals that contain the unshared pairs of the oxygen and sulfur atoms. According to the data from the molecular diagrams, like other polyhalopyridines, the carbon atoms in the 2 position

TABLE 1. Dipole Moments of 4-Substituted Tetrabromopyridines
4-X-C₅Br₄N*

Substituent X	$w \times 10^5$	$1/d$	ϵ_s	α	β	$P_{2\infty}$	R_D	μ
SH	0	1,1376	2,290	1,772	-0,784	185,9	62,8	2,34 †
	655	1,1335	2,303					
	1385	1,1281	2,313					
	2245	1,1218	2,330					
	2539	1,1188	2,335					
OH	0	0,9735	2,209	2,244	-0,595	204,3	62,6	2,58
	1031	0,9672	2,230					
	1888	0,9616	2,250					
	2784	0,9564	2,271					
	3825	0,9508	2,296					
	4768	—	2,316					
	0	0,9745	2,209					
993	0,9679	2,257						
1906	0,9616	2,299						
2877	0,9549	2,342						
3728	0,9513	2,383						
4629	0,9441	2,429						
NH ₂	0	0,9745	2,209	7,074	-0,687	539,4	58,1	4,83
	422	0,9713	2,240					
	700	0,9702	2,258					
	971	0,9690	2,280					
	1894	0,9615	2,343					
Br	0	0,9731	2,209	1,342	-0,631	151,2	62,4	2,01
	1016	0,9673	2,221					
	1943	0,9609	2,235					
	2879	0,9545	2,250					
	3788	0,9491	2,262					
	4698	—	2,273					

*The w values are the weight concentrations of the solutions, $1/d$ is the specific volume in cubic centimeters per gram, ϵ_s are the dielectric permeabilities of the solutions, α is the slope of the dependence $\epsilon_s = f(w)$, β is the slope of the dependence $1/d = f(w)$, $P_{2\infty}$ is the molecular polarization at infinite dilution in cubic centimeters, R_D is the molecular refraction in cubic centimeters, and μ is the dipole moment in debyes.

†In benzene solutions.

TABLE 2. Dipole Moments of Polyhalo-Substituted Pyridines*

Compound	$w \times 10^5$	$1/d$	ϵ_s	α	β	$P_{2\infty}$	R_D	μ
C ₅ Cl ₅ N	0	0,9736	2,209	1,384	-0,378	100,3	47,9	1,53
	902	0,9703	2,221					
	1901	0,9656	2,234					
	2843	0,9633	2,249					
	3784	0,9593	2,262					
	4623	0,9561	2,273					
C ₅ F ₅ N	0	0,9736	2,209	0,599	-0,335	47,8	13,6	1,26
	1029	0,9736	2,216					
	1946	0,9682	2,219					
	2885	0,9645	2,226					
	3806	0,9602	2,233					
	4669	—	2,237					
C ₅ H ₅ N	0	0,9734	2,209	8,154	0,095	130,6	23,8	2,24
	1046	0,9749	2,293					
	2002	0,9753	2,370					
	2901	0,9758	2,443					
	3767	0,9773	2,514					
	4611	0,9778	2,585					

*The symbols are the same as in Table 1.

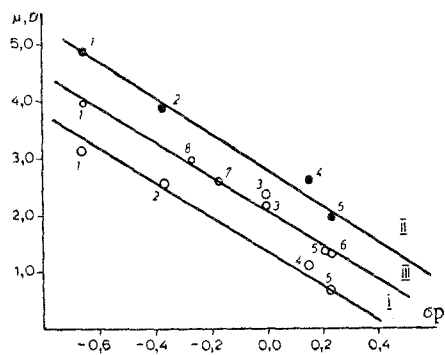


Fig. 3

Fig. 3. Dependence of the dipole moments on the σ_p constants of the substituents in the 4 position of the pyridine ring: I) calculated μ values for 4-substituted tetrabromopyridines: 1) NH_2 ; 2) OH ; 3) H ; 4) SH ; 5) Br ; II) experimental μ values for 4-substituted pyridines (according to the data in [8]): 1) NH_2 ; 2) OCH_3 ; 3) H ; 4) SH ; 5) Br ; 6) Cl ; 7) CH_3 ; 8) OCH_3 .

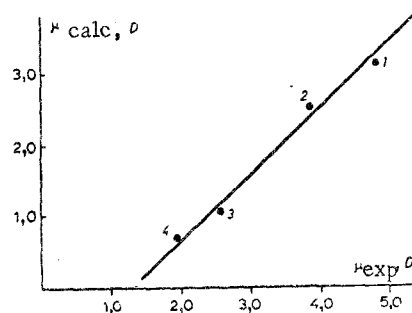


Fig. 4

Fig. 4. Comparison of the dipole moments obtained experimentally (μ_{exp}) and the values calculated by the CNDO/2 method (μ_{calc}): 1) NH_2 ; 2) OH ; 3) SH ; 4) Br .

of the ring are the most electron-deficient atoms in pentabromopyridine; however, according to the data in [12-13], the attack by the nucleophilic agent takes place primarily in the 4 position, and substitution occurs in the 2 position only for bulky substituents because of steric hindrance.

It is known that the Hammett equation is applicable to 4-substituted pyridines [14]; a linear relationship exists between the charge on the heteroatom and the σ_p substituent constants in most cases. This relationship for the examined compounds is presented in Fig. 2, from which it is apparent that the effect of substituents in 4-substituted tetrabromopyridines is similar to the effects in 4-substituted pyridines. Generally speaking, the charges on the heteroatom of pyridine and polyhalopyridines do not differ as substantially as one might have assumed. When the hydrogen atoms of the pyridine ring are replaced by halogen, the shift of the electron density via an inductive mechanism is compensated to a certain degree by the π -dative effect of the halogen atoms. Nevertheless, the changes in the dipole moment in this series are quite large (see Tables 1 and 2). These changes in the dipole moments of perhalo-substituted pyridines can be explained if one examines the two components of the dipole moment, one of which, viz., μ_1 , depends on the distribution of the charges in the molecule, the other of which, viz., μ_2 , reflects the atomic polarization moments, i.e., the character of the hybridization of the orbitals of the atoms of this molecule. In compounds of the pyridine series the chief role is played by the atomic polarization moment of the nitrogen atom, or, more precisely, the s character of the orbital of the unshared pair of electrons. The s contribution will be maximal in the case of perfluoropyridine, whereas it is minimal in the case of unsubstituted pyridine [2]. In the series of 4-substituted tetrabromopyridines the μ_2 component remains virtually unchanged, and the nature of the substituent in the 4 position of the ring consequently has the chief effect on the magnitude of the dipole moment.

It is known that a linear relationship exists between the dipole moments and the corresponding σ constants for disubstituted benzenes with one fixed substituent [14]. In the given case the nitrogen atom can be regarded as a fixed substituent, and between the dipole moments and the Hammett σ constants one should then expect a linear relationship, which is also presented in Fig. 3. For comparison, the experimental dipole moments for the same series of 4-substituted pyridines are presented in Fig. 3. It follows from the symbatic character of the change in these dipole moments that the transmission of the electronic effects does not undergo substantial changes in the case of bromination of the pyridine ring.

The relationship between the experimental and calculated dipole moments is presented in Fig. 4. It is difficult to expect better agreement between these values for molecules that contain atoms of the fourth period.

We also compared the experimental dipole moments of perbromo- and perchloro-substituted pyridines with the μ_{add} values calculated by the additive vector scheme:

	μ_{exp}	μ_{add}	$\Delta\mu = \mu_{\text{exp}} - \mu_{\text{add}}$
$\text{C}_5\text{Cl}_5\text{N}$	1.53	1.57	0.05
$\text{C}_5\text{Br}_5\text{N}$	2.01	1.51	0.50

The deviations of the μ_{add} values from the μ_{exp} values should evidently be regarded as satisfactory, since the $\Delta\mu$ values are of the same order of magnitude even for halogen-substituted benzenes [16]. The principal reason for the deviation in the μ values on passing from pentachloro- to pentabromopyridine consists in the mutual polarization of the halogen atoms and the corresponding change in the moments of the C-Hal bonds. At least two factors must be noted for polyhalopyridines. The most important is the effect of the hybridization dipole moment of the nitrogen atom [17]. The second most important factor is the possible distortion of the geometry and the change in the bond angles as the number of halogen atoms is increased and their size increases.

However, it follows from the results presented above that one can disregard the effect of these factors if the analysis of the electronic structure is carried out in a series of similarly constructed compounds.

EXPERIMENTAL

The measurements of the dielectric permeabilities (ϵ_s) of the solutions were made in a thermostatted cell at 298°K. The cell was a glass vessel with two platinum, coaxial, cylindrical electrodes with an overall surface area of 6.5 cm². The volume of the cell was ~ 5 cm³. Thermostatting of the solutions in the cell was realized by means of a jacket into which the transformer oil from a U-10 ultrathermostat was fed. The thermostating accuracy was $\pm 0.05^\circ\text{C}$. The ϵ_s values were recorded by means of an R-589 bridge. The densities of the solutions were determined by a gravimetric method in a modified Sprengel-Ostwald pycnometer. The refractive indexes (n_D) of the solutions were measured with an IRF-23 standard refractometer.

The dependences of the dielectric permeabilities and the specific densities of the solutions on their weight concentrations were linear up to 5 wt. %, and this made it possible to determine the slopes, viz., α and β , respectively. The total polarizations were calculated from the α and β values by the Halverstadt-Kumler method [7]. The molecular refractions (R_D) of the investigated substances were found either from the results of measurements of the dipole moments and the densities of the solutions by the method in [8] or were calculated from the refractions of the atomic groups [9]. The error in the determination of the dipole moments by the method described did not exceed ± 0.05 D. The principal results of the measurements of the dipole moments (μ) are presented in Tables 1 and 2. As standards we measured the μ values of bromobenzene and pyridine in solutions in benzene and dioxane. The dipole moments obtained were in good agreement for $\text{C}_6\text{H}_5\text{N}$ with $\mu_{\text{lit}} = 2.22$ and $\mu_{\text{exp}} = 2.24$ D; for $\text{C}_6\text{H}_5\text{Br}$, $\mu_{\text{lit}} = 1.52$ and $\mu_{\text{exp}} = 1.50$ D in benzene, and $\mu_{\text{lit}} = 1.61$ and $\mu_{\text{exp}} = 1.60$ D in dioxane. In view of the low solubilities of the investigated compounds in benzene, the μ values were measured in dioxane (according to the data in [10], the compounds are monomeric in this solvent). All of the substances were purified by two distillations or recrystallizations. The solvents were purified by the standard methods described in [11].

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¹³C NMR SPECTRA OF 5-SUBSTITUTED 8-MERCAPTOQUINOLINES

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The increments of the substituents were determined from the ¹³C NMR spectra of 5-substituted quinolines. It is shown that the increments correlate with those in benzenes, as well as with the Swain-Lupton constants. The ¹³C chemical shifts of some 5-substituted 8-mercapto-, 8-(methylthio)-, and 8-hydroxyquinolines were investigated. Their values are in satisfactory agreement with the additive contribution of the increments of the substituents. The deviations from additivity are associated with the steric hindrance to interaction of the substituents with the ring.

In a continuation of our studies of the electronic structures of quinoline and its derivatives in the present investigation we examined the ¹³C NMR spectra of 5-methyl-, 5-fluoro-, 5-chloro-, 5-bromo-, 5-iodo-, 5-(methylthio)-, 5-(pentylthio)-, 5-methoxy-, and 8-mercaptoquinoline (I-VIII) and 8-(methylthio)quinoline (IX-XVI), 5,8-dimercaptoquinoline (XVII), and 5-(ethylthio)-8-(methylthio)quinoline (XVIII), as well as 5-(methylthio)-, 5-(ethylthio)-, and 5-(propylthio)-8-hydroxyquinoline (XIX-XXI). The ¹³C NMR spectra of quinoline (XXII) and 8-mercapto-, 8-(methylthio)-, 8-hydroxy-, and 5-(methylthio)quinoline (XXIII-XXVI) were previously examined in [1, 2]. The increments of the substituents in the 5 position of the quinoline ring were determined from the ¹³C NMR spectra of 5-methyl-, 5-fluoro-, 5-chloro-, 5-bromo-, 5-iodo-, 5-amino-, and 5-mercaptoquinoline (XXVII-XXXIII). The ¹³C chemical shifts, the assignment of which was made on the basis of the spectra without decoupling of the protons (with the Overhauser nuclear effect) and the spectra with extrarésonance suppression of the ¹³C-¹H spin-spin coupling, are presented in Tables 1-3.

TABLE 1. ¹³C Chemical Shifts of 5-Substituted Quinolines

Compound	δ , ppm								
	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
XXVIII	151,6	121,5	129,0	158,2	110,6	129,2	125,9	149,5	119,4
XXIX	151,3	122,1	132,7	131,6	126,9	129,4	129,4	149,3	126,6
XXX	151,3	122,5	135,5	122,3	130,7	129,8	129,9	149,4	127,9
XXXI	151,5	123,1	140,6	99,2	138,1	130,8	131,0	149,2	130,8
XXVII	150,2	121,0	132,5	134,9	127,3	129,4	128,9	149,1	127,9
XXVI	151,1	121,3	133,0	137,5	124,5	129,7	127,7	149,0	127,7
XXXIII	151,0	121,6	133,8	129,0	129,9	129,5	128,8	149,0	128,2
XXII	150,7	121,6	136,4	128,4	127,0	129,9	129,9	148,8	128,8
XXXII	150,6	119,8	131,0	145,5	109,2	130,8	118,6	150,3	119,1

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