INFLUENCE OF AZASUBSTITUTION ON THE ELECTRONIC ABSORPTION SPECTRA OF PHTHALOCYANINS

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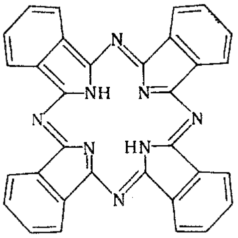
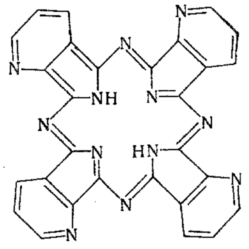
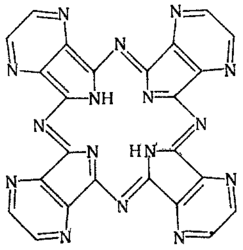
UDC 541.124:543.422.27:547.861

We showed earlier [1] that in the series of phthalocyanins (Pc), tetra-2,3-pyridinoporphyrazine (Py-2,3), tetra-2,3-pyrazinoporphyrazine (Pz), a hypsochromic shift of the long-wave absorption maximum in organic solvents is observed


Pc


Py-2,3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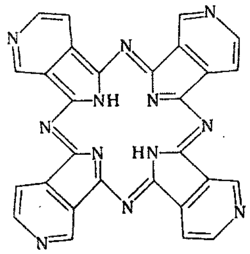

Py-3,4

At the same time, in the series of tetraaza-Pc, the long-wave absorption maximum depends substantially on the position of the nitrogen atoms with respect to the macrocycle as well: the electronic spectrum of tetra-3,4-pyridinoporphyrazine (Py-3,4), in contrast to Py-2,3, is identical in the visible spectrum with the spectrum of the corresponding Pc [2]. In this communication we compared the electronic absorption spectra of analogs of Pc and their tert-butyl derivatives with the spectra of the corresponding Pc in a broad spectral interval (Table 1) and present a theoretical explanation of the influence of azasubstitution.

We synthesized tert-butyl-substituted azaanalogs possessing, like the corresponding tert-butyl-substituted Pc [3], high solubility in organic solvents, which made it possible to investigate the previously unstudied UV portion of their electronic spectrum. Thus, the interaction of the polyamide of 6-tert-butylcinchomeronic acid [4] with the corresponding chlorides in the presence of urea yielded vanadyl (I) and cobalt (II) complexes of tetra-3,4-(6-tert-butylpyridino)porphyrazine. Analogously to PcH_2 [5], the interaction of 5-tert-butyl-2,3-dicyanopyrazine (III) with lithium amylate in amyl alcohol yielded nonmetal-containing tetra-2,3-(5-tert-butylpyrazino)porphyrazine (IV); we described the synthesis of metallic complexes from the corresponding acids earlier [6]. The dinitrile (III) was synthesized by condensation of tert-butyl-glyoxal [7] with diaminomaleodinitrile (a tetramer of hydrogen cyanide) [8]

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1976-1980, September, 1973. Original article submitted July 12, 1972.

TABLE 1. Absorption Maxima of Phthalocyanins and Their Azaanalogs

Compound	Solvent	λ_{max} (lg ε),nm *			
		1	2	3	4
Vanadyl Pc	DMSO	685	618,5	346,5	290sh
Vanadyl 6-tert-butyl-Py-3,4	DMSO	680	616	345	—
	Benzene	700 (5,61)	630 (4,98)	342 (5,18)	—
Vanadyl Py-2,3 [1]	DMSO	645	585	340	—
Vanadyl Pz [1]	DMSO	635	580	345	290
Vanadyl 5-tert-butyl-Pz [6]	DMSO	634	578	343	292
	$CHCl_3$	645 (5,14)	586 (4,42)	343 (4,90)	292 (4,71)
Cobalt Pc	DMSO	663	597	329	—
Cobalt 6-tert-butyl-Py-3,4	DMSO	660	595	327	—
	$CHCl_3$	672	605	325	—
Tetra-4-tert-butyl-Pc [3]	$CHCl_3$	705, 671	645,605	342	—
5-tert-Butyl-Pz	$CHCl_3$	653 (5,08) 617 (4,95)	570 (4,34)	340 (5,02)	—

*The numbers denote absorption bands: 1) λ_1; 2) its vibrational satellite; 3) λ_2 (Soret band); 4) λ_3.

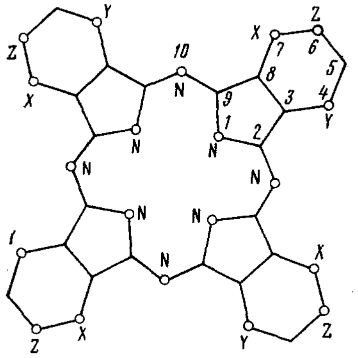
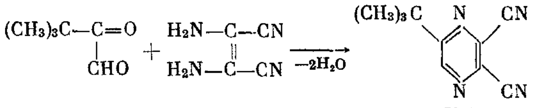


Fig. 1. Numeration of the atoms of the model of phthalocyanin (X, Y, Z = CH) and its azaderivatives (X = N; X, Y = N; Z = N).



(III)

From the data of Table 1, considering the absence of an influence of the tert-butyl groups on the nature of the spectrum, the following conclusion can be drawn: in contrast to the long-wave band λ_1 and its vibrational satellite, the bands in the UV region in the case of azasubstitution in the Pc molecule experience practically no shift.

The electronic structure of Pc and its metallic complexes has been calculated repeatedly by various methods (see, for example, [9, 10]). The purpose of this investigation was to explain the behavior of the long-wave absorption maximum (λ_1) described above, corresponding to the transition $a_{1u}(a_u) \rightarrow e_g(\varepsilon_1)$, and the Soret band ($\lambda_2$), corresponding to the transition $a_{2u}(a_u) \rightarrow e_g(\varepsilon_2)$, in the spectra of metallic complexes of phthalocyanin and its azaderivatives.

For this purpose, the vanadyl complexes of Pc, Pz, Py-2, 3, and Py-3, 4 were calculated by the Hückel method within the framework of the π-electronic approximations.* These isoelectronic systems each have 42 π-electrons (36 in the macroring of phthalocyanin and in the outer six-membered rings, as well as 6 π-electrons of the four inner nitrogen atoms). It was suggested that Pz and Pc have the symmetry D_{4h}, while Py-2, 3 and Py-3, 4 have the symmetry C_{4h} (Fig. 1). Our variation of the system of parameters showed that qualitatively the results of the calculation do not depend on the selection of the parameters, within rather broad limits. In this communication we discussed the results obtained with the parameters of [11]. For the four inner nitrogen atoms, we took the parameters of pyrrole ($\alpha_N = \alpha + \beta$, $\beta_{CN} = 0.9\,\beta$), and for the four remaining nitrogen atoms those of pyridine ($\alpha_N = \alpha + 0.4\,\beta$, $\beta_{CN} = \beta$). The resonance integral β was determined according to the energies of the first transitions ε_1 by the method of least squares.

The energy levels of the systems under consideration obtained from the calculation are cited in Table 2. Table 3 presents the values of the energies of the transitions ε_1 and ε_2, as well as the wavelengths λ_1 and λ_2 corresponding to them. It is evident that both the hypsochromic shifts of the band λ_1 in the series Pc, Py-2, 3, and Pz, as well as its insensitivity to azasubstitution in the 3, 4-position, are in quantitative agreement with the results of the calculation. The band of the second transition λ_2 in all the compounds is very broad; moreover, it overlaps with the more short-wave band λ_3; therefore, it is difficult to judge

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*The orbitals of the metal were not included in the calculation. The inductive influence of the metal on the inner nitrogen atoms was considered parametrically by increasing the coulombic integral.

TABLE 2. Energy Levels (in units of β)

Symmetry of MO*	Scheme of levels†	Pc	Py-2,3	Pz	Py-3,4
$b_{2u}(b_u)$	——	—0,603	—0,586	—0,538	—0,553
e_g	—— ——	—0,177	—0,158	—0,141	—0,154
$a_{1u}(a_u)$	⇅	0,295	0,339	0,372	0,320
$a_{2u}(a_u)$	⇅	0,673	0,674	0,675	0,680
e_g	⇅ ⇅	0,900	0,994	1,000	0,915

*The notations in parentheses correspond to the symmetry C_{4h} of pyridine analogs.

†The remaining vacant and occupied levels are not cited.

TABLE 3. Energies of Transitions ε_1 and ε_2 (in units of β) and Wavelengths λ_1 and λ_2 Corresponding to Them (in nm)

Compound	Calculation				Experiment	
	ε_1	λ_1	ε_2	λ_2	λ_1	λ_2
Pc	0,472	683	0,850	391	685	346
Py-2,3	0,497	651	0,832	399	645	340
Pz	0,513	632	0,816	407	635	345
Py-3,4	0,474	680	0,834	398	680	345

the exact position of the maximum. It can only be asserted that it is little shifted from the azasubstitution. This is also in good agreement with the calculation (see Table 3).

The causes of the peculiarities of the behavior of the spectra of metallic complexes of Pc in the case of azasubstitution become understandable in a consideration of the shape of the molecular orbitals, among which there are transitions ε_1 and ε_2 (Table 4; the numeration of the atomic π-orbitals is given in Fig. 1). The nature of these orbitals is practically unchanged by azasubstitution. The molecular orbitals e_g to which a π-electron is transferred correspond to a double degenerate level. These orbitals encompass all the atoms of the system, primarily the atoms of the inner 16-membered ring of Pc* (φ_1, φ_2, φ_9, φ_{10}). Naturally, azasubstitution in the benzene rings only slightly lowers its energy. The molecular orbital $a_{1u}(a_u)$, from which the transition ε_1 occurs, is constructed primarily from the orbitals of eight carbon atoms of the inner ring of Pc (φ_2, φ_9). The orbitals of the nitrogen atoms of the inner ring (φ_1, φ_{10}) do not enter into this molecular orbital. The participation of the atomic orbitals φ_4 and φ_7 of the six-membered rings is rather appreciable. Therefore, the energy of the orbital $a_{1u}(a_u)$ decreases to a far greater degree than the energy of the orbital e_g as the carbon atoms 4 and 7 are replaced by nitrogens. From the ratio of the coefficients of the atomic orbitals φ_4 and φ_7, on the one hand, and φ_5 and φ_6, on the other, it is also understandable why the band λ_1 is relatively insensitive to azasubstitution of the carbon atoms 5 and 6.

Thus, the peculiarities of the hypsochromic shifts of the band λ_1 in the case of azasubstitution are entirely explained by the nature of the molecular orbitals between which this transition occurs.

The molecular orbital $a_{2u}(a_u)$ for all four molecules is constructed primarily from the π-orbitals φ_1 and φ_{10} of the eight nitrogen atoms of the inner ring of Pc. Therefore, its energy depends substantially on the selection of the parameters of the inner nitrogen atoms. As can be seen from Table 3, the parameters of pyrrole that we took for these nitrogens [11] insufficiently reflect the inductive influence of the metal. Evidently the use of the coulombic integral $\alpha_N = \alpha + 1.2\,\beta$ (according to [9]) leads to better agreement with the experiment. Since all the remaining atomic orbitals participate little in $a_{2u}(a_u)$, the insensitivity of the energy of this molecular orbital to the introduction of nitrogen into the benzene rings is understandable (see Table 2). Since the orbital e_g is also relatively insensitive to azasubstitution, the weak sensitivity of the band λ_2 to the introduction of supplementary nitrogens is understandable.

EXPERIMENTAL

Vanadyl Complex of Tetra-3,4-(6-tert-butylpyridino)porphyrazine (I). A mixture of 0.2 g of the hemiamide of 6-tert-butylcinchomeronic acid [7] with mp 184°, 1 g urea, 0.1 g VCl_3, and the catalytic amount of ammonium vanadate was slowly heated to 240°, exposed at this temperature for 15 min, cooled, washed

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*Here and henceforth, the atomic orbitals are indicated for one fragment.

TABLE 4. Molecular Orbitals between Which the Transitions ε_1 and ε_2 Occur*

MO		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9	φ_{10}
Pc	$\psi(a_{2u})$	0,282	—0,051	0,086	0,023	—0,070	—0,070	0,023	0,086	—0,051	—0,374
	$\psi(a_{1u})$	0	—0,271	—0,080	0,168	0,130	—0,130	—0,168	0,080	0,271	0
	$\psi(e_g)$	0,132	0,127	0,171	—0,051	—0,162	0,080	0,148	—0,106	—0,300	0,040
		0,171	—0,277	—0,065	0,140	0,040	—0,147	—0,015	0,149	0,053	—0,313
Pz	$\psi(a_{2u})$	0,284	—0,051	0,082	0,024	—0,075	—0,075	0,024	0,082	—0,051	—0,372
	$\psi(a_{1u})$	0	—0,288	—0,107	0,141	0,103	—0,103	—0,141	0,107	0,288	0
	$\psi(e_g)$	—0,001	0,267	0,184	—0,109	—0,125	0,126	0,107	—0,184	—0,265	0,223
		0,250	—0,144	0,036	0,105	—0,093	—0,092	0,106	0,034	—0,147	—0,220
Py-2,3	$\psi(a_u)$	0,282	—0,044	0,089	0,025	—0,072	—0,073	0,023	0,080	—0,058	—0,373
	$\psi(a_u)$	—0,001	—0,280	—0,081	0,143	0,129	—0,100	—0,163	0,109	0,281	—0,013
	$\psi(e_g)$	0,048	0,232	0,176	—0,076	—0,164	0,102	0,148	—0,184	—0,295	0,187
		0,217	—0,190	0,022	0,112	—0,039	—0,106	0,056	0,075	—0,089	—0,256
Py-3,4	$\psi(a_u)$	0,294	—0,063	0,066	0,027	—0,047	—0,059	0,030	0,080	—0,042	—0,373
	$\psi(a_u)$	0,001	—0,272	—0,102	0,168	0,155	—0,118	—0,146	0,071	0,270	0,014
	$\psi(e_g)$	0,056	0,217	0,199	—0,101	—0,184	0,129	0,112	—0,146	—0,289	0,140
		—0,211	0,211	0,017	—0,112	0	0,112	—0,062	—0,102	0,060	0,283

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*The values of the coefficients are cited for the atomic orbitals of atoms of one fragment (atoms 1-10). The values of the coefficients for atomic orbitals corresponding to the remaining fragments are obtained from considerations of symmetry.

with boiling water, the complex extracted with boiling benzene, chromatographed on Al_2O_3 (activity V), the blue band eluted with chloroform, and the eluate evaporated. Yield of the complex (I) 0.02 g (18%).

The cobalt complex of tetra-3,4-(6-tert-butylpyridino)porphyrazine (II) was produced analogously from the hemiamide of cinchomeronic acid, cobalt chloride, and ammonium molybdate (as a catalyst) in a urea melt. Yield of (II) 20%.

5-tert-Butyl-2,3-dicyanopyrazine (III). To a solution of 0.3 g diaminomaleodinitrile [8] with mp 179-181° and 0.6 g tert-butylglyoxal [7] in 10 ml of alcohol we added 1 ml glacial CH_3COOH, boiled for 1.5 h, then evaporated to dryness under vacuum. The residue was treated with boiling benzene, the benzene extract chromatographed on Al_2O_3, (III) washed with chloroform, and the eluate evaporated to dryness. Yield of (III) 0.22 g (40%), mp 64-65° (from alcohol). Found: N 29.88%. $C_{10}H_{10}N_4$. Calculated: N 30.09%.

The peaks 186 (M^+), 171 ($M^+ - 15$), 143 ($M^+ - 43$), as well as the metastable peak 199.5 ($143^2/171$), due to fragmentation with elimination of an ethylene molecule, were detected in the mass spectrum of (III).

Tetra-2,3-(5-tert-butylpyridino)porphyrazine (IV). To a solution of 1.5 mmoles lithium amylate in 5 ml abs. amyl alcohol we added 5 mmoles (III) in small portions with mixing. The mixture was boiled for 1 h, and evaporated to dryness under vacuum. The residue was reprecipitated from conc. H_2SO_4, chromatographed on silica gel, eluting the blue-green fraction with chloroform, and the eluate evaporated to dryness. (IV) was obtained in a yield of 15%.

The authors would like to thank N. P. Gambaryan for his discussion of the results of the calculation.

CONCLUSIONS

1. Some new tert-butyl-substituted azaanalogs, possessing increased solubility in organic solvents, were synthesized for a study of the influence of azasubstitution on the electronic absorption spectra of phthalocyanin.

2. Azasubstitution in the phthalocyanin molecules does not change the position of the absorption bands in the near UV region, while the long-wave absorption bands undergo a substantial hypsochromic shift, the value of which depends on the number of supplementary nitrogen atoms and on their position.

3. These peculiarities of the spectra of phthalocyanins are explained by the nature of the molecular orbitals, between which the corresponding π-electronic transitions occur.

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