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UNSATURATED CHLORO-SUBSTITUTED DINITRILES IN THE SYNTHESIS OF PORPHYRAZINES

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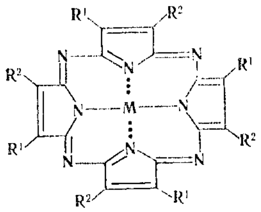
UDC 547.979.733.07:543.422.6

Chloro- and alkoxy-substituted porphyrazines were obtained in the reaction of mono- and dichloromaleo(fumaro)nitriles with metal chlorides or alkoxides. The structures of the synthesized compounds were confirmed by their electronic absorption spectra.

The introduction of halogen atoms into the benzene rings of phthalocyanines is widely used for the preparation from them of photostable green pigments. In the present communication we describe the synthesis of previously unknown chloro-substituted porphyrazines — structural analogs of phthalocyanines — by condensation of mono- (I) and dichloromaleo(fumaro)nitrile (II) with metal chlorides and alkoxides. Dinitriles I and II were also the starting compounds in the synthesis of alkoxy-substituted porphyrazines.



III M=VO, R¹=Cl, R²=H; IV M=VO, R¹=R²=Cl; V M=Mg, R¹=OC_5H_{11}, R²=H; VI M absent

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Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1645-1646, December, 1982. Original article submitted February 23, 1982.

0009-3122/82/1812- 1269$07.50

TABLE 1. Characteristics of the Substituted Porphyrazines

Compound	Solvent	UV spectrum λ_{max}, nm (log ε)	Found, %			Empirical formula	Calc., %		
			C	H	N		C	H	N
III	C_6H_6	606 (4,79), 552 (4,25), 350 (4,51)*	37,0	0,7	21,4	$C_{16}H_4Cl_4N_8OV$	37,2	0,8	21,7
IV	o-Dichlorobenzene	612 (4,69), 583 sh (4,04), 556 (3,74), 346 (4,42)*	29,2	—	17,0	$C_{16}Cl_8N_8OV$	29,4	0,0	17,1
V	$CHCl_3$	608 (4,70), 558 (4,26), 325 (4,93)	63,1	7,2	16,6	$C_{36}H_{48}MgN_8O_4$	63,5	7,2	16,4
VI	$CHCl_3$	644 (4,67), 590 sh (4,25), 572 (4,51), 329 (4,81)	66,2	7,8	18,1	$C_{36}H_{50}N_8O_4$	65,8	7,7	17,4
VII	$CHCl_3$	518 (4,80), 598 (4,86), 550 sh (4,28), 352 (4,92)	43,5	2,8	Cl 30,0	$C_{26}H_{22}Cl_6MgN_8O_2$	43,6	3,1	Cl 29,8

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*UV spectrum of vanadyl tetra(tert-butyl)porphyrazine [1] in hexane, λ_{max} (log ε): 594 (5.09), 543 (4.19), and 342 nm (4.76).

Vanadyl complexes of tetra- (III) and octachloroporphyrazine (IV) are formed in the reaction of dinitriles I and II with vanadium trichloride in the presence of ammonium molybdate in trichlorobenzene or 1-chloronaphthalene. Compound III is quite soluble in low-boiling solvents such as benzene or chloroform, while perchloro-substituted IV is soluble only in high-boiling solvents such as 1-chloronaphthalene and di- and trichlorobenzene. The increased solubility of III is probably associated with the lower symmetry of the molecule, which is also observed in the case of chloro-substituted phthalocyanines [1]. Magnesium complexes with total or partial substitution of the chlorine atoms are formed when magnesium amylate is used as the complexing agent. Thus for I we obtained magnesium tetraamyloxyporphyrazine (V), which upon refluxing in glacial acetic acid was converted to a metal-free compound (VI). However, a mixture of substitution products, from which the diamyloxyhexachloro derivative of magnesium (VII) was isolated by chromatography, is formed in the reaction of II with magnesium amylate in amyl alcohol.

A great similarity to the spectra of tert-butyl-substituted porphyrazines [2] was noted in the electronic absorption spectra of III-VI in the visible and near-UV regions over the 240-700 nm range. However, the presence of alkoxy groups or chlorine atoms attached to the macrocyclic ligand leads to a bathochromic shift of the long-wave absorption band. In the case of VII the band is a doublet with maximum at 618 and 598 nm; this is associated with a decrease in the symmetry of the molecule when two alkoxy groups are introduced into the pyrrole fragments. The introduction of chlorine atoms into the porphyrazine molecules also leads to an appreciable bathochromic shift of the band in the UV region (see Table 1).

EXPERIMENTAL

The electronic absorption spectra of $\sim 10^{-5}$ M solutions were recorded with a Hitachi-356 spectrophotometer.

Vanadyl Tetrachloro- (III) and Octachloroporphyrazine (IV). A mixture of 0.3 g (2.66 mmole) of dinitrile I, 0.3 g (1.9 mmole) of vanadium trichloride, and 0.01 g (0.005 mmole) of ammonium molybdate in 3 ml of trichlorobenzene was refluxed for 3 h, after which it was chromatographed on silica gel in chloroform to give 0.1 g (34%) of III with R_f 0.5.

Compound IV was similarly obtained in 37% yield from dinitrile II in refluxing 1-chloronaphthalene with subsequent extraction with o-dichlorobenzene.

Magnesium Tetraamyloxyporphyrazine (V). A mixture of 1 g (8.88 mmole) of I and magnesium amylate (from 0.2 g of magnesium) in 10 ml of amyl alcohol was refluxed for 4 h, after which it was diluted with aqueous ethanol (1:1), and the resulting precipitate was separated and washed with ethanol until the filtrate was colorless. The residue was chromatographed on silica gel with chloroform–ethanol (100:1) to give 0.3 g (29%) of V with R_f 0.17.

Tetraamyloxyporphyrazine (VI). A solution of 0.1 g (0.16 mmole) of V in 4 ml of glacial acetic acid was refluxed for 1 h, after which it was cooled and made alkaline with 10% sodium carbonate solution. The resulting precipitate was separated and chromatographed on silica gel by elution with chloroform to give 0.04 g (41%) of VI with R_f 0.5.

Reaction of II with Magnesium Amylate. A mixture of 1 g (6.78 mmole) of nitrile II and magnesium amylate (from 0.1 g of magnesium) in 5 ml of amyl alcohol was refluxed for 3 h, after which it was poured into aqueous alcohol (1:1). The resulting precipitate was separated and washed with aqueous alcohol until the filtrate was colorless, and the residue was chromatographed on silica gel with chloroform–ethanol (100:1) to give 0.045 g (4%) of VII with R_f 0.31.

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THREE-DIMENSIONAL STRUCTURE OF 3-ACYLINDOLES

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UDC 547.756.07:543.422.4

On the basis of a comparison of the experimental dipole moments with the calculated values, as well as data from the UV, IR, and PMR spectra, it is shown that 3-acylindoles exist in the form of equilibrium mixtures of the planar S-cis and S-trans conformers with preponderance of the latter.

There are presently various methods for the preparation of 3-acylindoles, and these compounds are often used as starting substances for the synthesis of many indole derivatives. However, clearly insufficient study has been devoted to their three-dimensional structures, whereas they do in a number of cases determine the reactivities of these compounds and the possibility of the realization of certain transformations. With respect to the investigation of the three-dimensional structures of 3-acylindoles, one should mention only the study of some 3-formylindoles by NMR spectroscopy [1], as well as the use of shift reagents [2] for the determination of the configuration of 3-acetyl-1-methylindole.

We have investigated an extensive set of 3-acylindoles by various methods, and in the present paper we present the results of these studies.

IR Spectra

In both the solid state and in solutions [3] the carbonyl group of the investigated ketones absorbs in a region that is anomalous for aromatic ketones (Table 1). Of course, this band is made up of combination vibrations of the nitrogen atom–C_2–C_3 double bond–carbonyl group system. The magnitude of this frequency compels us to assume strong conjugation of the carbonyl group with the aromatic system of indole. This conjugation should be realized most fully in two planar variants of orientation of the carbonyl group (S-cis and S-trans).† Many of the ketones that we investigated (for example, V-VII and X-XIII) in the solid state (in mineral oil) have doublets at 1580-1640 cm^{-1}. The doublet character of the absorption vanishes on passing to solutions (in chloroform and dioxane), but the nonsymmetri-

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*Deceased

†Nomenclature that takes into account the mutual orientation of the carbonyl oxygen atom and the heteroatom is often used in the literature (for example, see [5]). It seems to us that it is more accurate to use the S-cis–S-trans nomenclature, which takes into account the mutual orientation of the double bonds, as was originally used for butadiene systems.

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0009-3122/82/1812-1271$07.50