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SYNTHESIS OF A NEW FOURTEEN-MEMBERED MACROHETEROCYCLIC SYSTEM BY MEANS OF A SUBSTITUTED 5-CHLOROPYRAZOLE

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UDC 541.572.54:547.773'779'898

A new fourteen-membered macrocyclic system was obtained by template cyclization of 4-(2-bromophenylazo)-5-chloro-3-methyl-1-phenylpyrazole with 2,2'-diaminoazobenzene in an aprotic solvent in the presence of nickel acetate and potassium carbonate.

5-Chloropyrazoles containing an azo group in the 4 position have increased reactivity in nucleophilic substitution reaction [1]. It is also known that a halogen atom in the ortho position relative to the azo group in aromatic azo compounds is readily replaced by substituted amino groups when the metal template method is used [2,3]. We used these facts in the the synthesis of a new 14-membered macroheterocyclic system containing a 5,12-dihydro-1,2,3, 8,9,12-hexaazatetradecyne ring starting from 4-(2-bromophenylazo)-5-chloropyrazole (I). 2, 2'-Diaminoazobenzene was used as the nucleophilic reagent, and the reaction was carried out in polar aprotic solvents in the presence of nickel (II) acetate and potassium carbonate. It was established that [10,21-dihydro-3-methyl-1-phenylpyrazole[4,5-c]tribenzo[f,j,m][1,2, 5,8,9,12]hexaazacyclotetradecynato(2−)N^4,N^{10},N^{15},N^{21}]nickel (II) and 5-{[2-(2-aminophenylazo)phenyl]amino-4-(2-bromophenylazo)-3-methyl-1-phenylpyrazolato}(2−)nickel (III) are formed at the very start of the reaction (III is present in relatively large amounts) in the course of the synthesis in Hexametapol (hexamethylphosphoric triamide). The amount of III subsequently gradually decreases. A somewhat different pattern is observed when the reaction is carried out in dimethylformamide (DMF): the amounts of II and III increase with time, but the amount of III does not subsequently decrease. It was established by special experiments that III is cyclized to complex III when it is heated in Hexametapol in the presence of nickel(II) acetate and potassium carbonate. This sort of process does not occur in DMF. It may be assumed that the successive replacement of chlorine and bromine and double (synchronous) nucleophilic substitution of these halogens proceed simultaneously and that double nucleophilic substitution is the only source of the macroheterocyclic system when the synthesis is carried out in DMF.

Macrocyclic chelate II is characterized by high stability, and the nickel ion is not freed under the influence of concentrated acids. Chelate III is demetallized to give free ligand IV even in dilute mineral acid.

The IR spectra of II do not contain characteristic bands in the region of the stretching vibrations of NH bonds. The IR spectrum of III has a characteristic band of NH-bond vibra-

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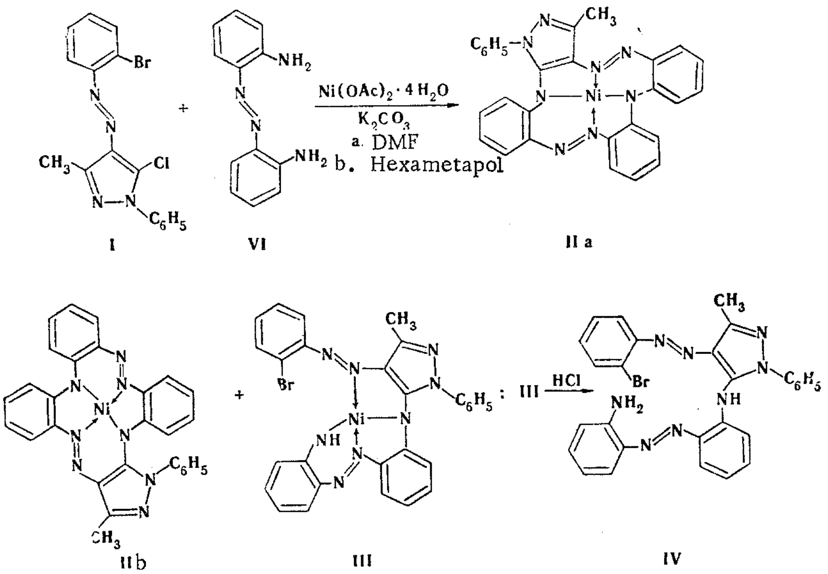
tions at 3353 cm^{-1}. A band of NH-bond vibrations at 3345 cm^{-1} and two bands of stretching vibrations of a NH_2 group at 3441 (ν_{sym}) and 3525 cm^{-1} (ν_{as}) are observed in the IR spectrum of IV.



According to the mass-spectral data, the mass numbers of the molecular ions of II, III, and IV are 527, 608, and 551; these values are in conformity with the calculated values and the values obtained by ebullioscopy.

The available data do not make it possible to make a precise choice between structures IIa and IIb. Recourse to special methods is required for this.

EXPERIMENTAL

The electronic spectra were recorded with an MPS-50L spectrophotometer. The IR spectra were recorded with a UR-20. The mass spectra were recorded with an AEI MS 905 mass spectrometer at an accelerating voltage of 10 kV, and ionizing voltage of 70 eV, and sample vaporization block temperatures of 180° (II and III) and 160° (IV) with direct introduction of the samples into the ionization region. The molecular weights presented in the experimental section were determined by ebullioscopy in chloroform solutions. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with elution by benzene (II, III) and chloroform (IV).

4-(2-Bromophenylazo)-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (V). This compound, with mp 198-199° (from acetone; mp 199-200° [2]), was obtained in 85.5% yield by diazotization of 2-bromoaniline and subsequent diazo coupling with 3-methyl-1-phenyl-5-pyrazolone in weakly alkaline media.

4-(2-Bromophenylazo)-5-chloro-3-methyl-1-phenylpyrazole (I). Triethylamine (14 ml) was added dropwise at room temperature to 35.7 g (0.1 mole) of pyrazole V and 300 ml of phosphorus oxychloride, after which the mixture was refluxed (at 110-115°) for 7 h. It was then cooled, and the resulting precipitate was removed by filtration and washed with three 30-ml portions of cold acetone to give 28 g of I. Vacuum distillation of the mother liquor gave ~100 ml of $POCl_3$. The residue was poured over 200 g of crushed ice, and the mixture was neutralized to pH 7 with 2 N NaOH solution. The resulting precipitate was removed by filtration, washed with 30 ml of cold acetone, and dried to give another 8 g of I. Recrystallization from acetone gave 34 g (88.8%) of pure I with mp 141.5-142.5°. Found: C 50.8; H 3.2; Cl 9.5; Br 21.1; N 14.9%; M 385. $C_{16}H_{12}BrClN_4$. Calculated: C 51.0; H 3.2; Cl 9.6; Br 21.3; N 14.9%; M 375.67.

2,2'-Diaminoazobenzene (VI) and 2,2'-Diaminoazoxybenzene (VII). These compounds were obtained by our modification of the method in [4]. In the reduction of O-nitroacetanilide with hydrazine hydrate in alkaline media, 10% palladium on carbon was used as the catalyst in place of Raney nickel. Reduction of the o-nitroacetamide and subsequent alkaline hydrolysis of the acetamido compounds gave 14 g (47.6%) of VI, with mp 132-133.5° (from ethanol), and 5.2 g (18.4%) of VII, with mp 114-115° (from carbon tetrachloride) (according to [4,5], VI has mp 133-134°, and according to [6], VII has mp 115°).

[10,21-Dihydro-3-methyl-1-phenylpyrazole[4,5-c]tribenzo[f,j,m][1,2,5,8,9,12]hexaazacyclotetradecynato-(2)N^4,N^{10},N^{15},N^{21}]nickel (II) and 5-{[2-(2-Aminophenylazo)phenyl]amino-4-(2-bromophenylazo)-3-methyl-1-phenylpyrazolato}-(2−)nickel (III). A) A mixture of 2.12 g (0.01 mole) of 2,2'-diaminoazobenzene, 3.75 g (0.01 mole) of I, 2.46 g (0.01 mole) of nickel (II) acetate tetrahydrate, 5.52 g (0.04 mole) of K_2CO_3, and 70 ml of DMF was refluxed for 8 h. The course of the reaction was monitored by TLC. The mixture was cooled and filtered, and the solid material was washed with water until the wash waters gave a negative test for halide ions. The solid was then dried and recrystallized from benzene—methanol (1:5) to give 0.6 g (11.4%) of brown-greenish finely crystalline II with mp 340-350° (dec.). The solubilities of the product in benzene, chloroform, acetone, and DMF ranged from $5 \cdot 10^{-2}$ to 10^{-3} M. It was only slightly soluble in carbon tetrachloride, methanol, ethanol, cyclohexane, and hexane. It was soluble in concentrated sulfuric acid (dilution or neutralization of the solution gave II) but insoluble in other mineral acids and water. Found: C 63.3; H 3.5; N 21.4; Ni 11.7%; M 551. $C_{28}H_{20}N_8Ni$. Calculated: C 63,8; H 3.8; N 21.2; Ni 11.1%; M 527.21. The nickel content was determined by the Deniget method [7]. Electronic spectrum (isooctane), λ_{max}, nm (log ε): 230 (4.21), 260 (4.18), 305 (4.15), 395 (3.87), 470 (4.08), 710 (3.34). The product had R_f 0.22.

The DMF solution remaining after separation of III was diluted with a threefold volume of water, and the resulting black precipitate was removed by filtration, dried, dissolved in 30 ml of benzene, and chromatographed with a column filled with silica gel (Chemapol L 100/160 μ) with elution with benzene. This procedure gave a fraction (A) containing primarily II, followed by a fraction (B) containing III. The solvent was removed from fraction A by distillation, and the resulting complex II was crystallized twice from benzene—methanol (1:5) to give 0.37 g of II. The overall yield of II was 0.97 g (17.1%). The solvent was removed from fraction B by distillation, and III was crystallized from benzene—petroleum ether (1:3) to give 0.52 g (10.3%) of III with mp > 240° (dec.). The solubilities of the product in benzene, chloroform, toluene, DMF, and acetone ranged from 10^{-1} to 10^{-2} M. The product was much less soluble in carbon tetrachloride, ethanol, methanol, hexane, and cyclohexane and was decomposed by mineral acids. It was insoluble in water. Found: C 55.6: H 3.7; Br 12.7; N 18.5; Ni 10.1%; M 624. $C_{28}H_{21}BrN_8Ni$. Calculated: C 55.4; H 3.5; Br 13.2; N 18.4; Ni 9.6%; M 608.12. Electronic spectrum (isooctane), λ_{max}, nm (log ε): 254 (4.23); 370 (4.05); 435 (3.83); 555 (3.24); 665 (3.16). The product had R_f 0.16.

B) The synthesis of II in Hexametapol (90 ml) was carried out similarly at 180° for 6 h. Recrystallization of the product gave 1.45 g (27.6%) of II. Only a small amount of III was formed. The yield of complex II was raised to 35% when the reaction was carried out in a stream of nitrogen.

C) Preparation of II by Cyclization of III. A 0.1-g sample of III was refluxed in 30 ml of hexametapol in the presence of 0.05 g of nickel (II) acetate tetrahydrate and 0.12 g of potassium carbonate for 3 h (the conversion of III to II was monitored by TLC). The reaction mixture was diluted with 100 ml of water, and the resulting precipitate was washed with water until carbonate and halide ions were no longer present in the wash waters. The product was then crystallized from benzene—methanol (1:5) to give 0.07 g (67.4%) of II.

5-{[2-(Aminophenylazo)phenyl]amino}-4-(2-bromophenylazo)-3-methyl-1-phenylpyrazole (IV). A 1.2-g (0.002 mole) sample of III was dissolved by heating at 60° in 100 ml of hydrochloric acid (1:1), and the resulting red solution was poured over 200 g of ice. The aqueous mixture was cooled to 10° and neutralized to pH 6-7 with 2 N NaOH solution. The resulting precipitate was dried, dissolved in 25 ml of benzene, and chromatographed with a column filled with silica gel (elution with chloroform). The chloroform was removed by distillation, and the residue was recrystallized from n-heptane to give 0.41 g (39.2%) of lamellar orange crystals of IV with mp 162-163°. The solubilities of the product in benzene, chloroform, toluene, acetone, and ether ranged from 10^{-1} to 10^{-2} M. It was less soluble in ethanol, carbon, tetrachloride, hexane, cyclohexane, and petroleum ether and insoluble in water. Found: C 61.1; H 3.7; Br 14.2; N 20.5%; M 565. $C_{28}H_{23}BrN_8$. Calculated: C 61.0; H 4.0; Br 14.5; N 20.4%; M 551.45.

Electronic spectrum (isooctane), λ_{max}, nm (log ε): 228 (4.52), 256 (4.43), 328 (4.41), and 400 (4.38). The product had R_f 0.68.

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o-TOSYLAMINO-SUBSTITUTED 2-ARYLBENZIMIDAZOLES

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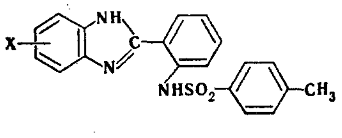
A number of o-tosylamino-substituted 2-arylbenzimidazoles were synthesized, and the effect of substituents on the position of the absorption bands of toluene solutions of the products was investigated. Except for the compound containing a nitro group, the investigated compounds fluoresce in the solid state and in toluene; an anomalously large Stokesian shift is characteristic for them.

An anomalously high Stokesian shift is characteristic for the fluorescence of a considerable number of compounds with an intramolecular hydrogen bond, and this makes it possible to use some of them as organic luminophores that are colorless in daylight [1-5]. Compounds with an intramolecular hydrogen bond in which the tosylamino group acts as the proton-donor group — specifically, 2-(tosylaminophenyl)-4H-3,1-benzoxazin-4-ones [6], 2-(2-tosylaminophenyl)-4(3H)-quinazolones [7], and 2-2(tosylaminophenyl)benzoxazoles [8] — have recently become well known.

We have synthesized and investigated o-tosylamino-substituted 2-arylbenzimidazoles I and II (X = hydrogen or functional substituents in the 5 or 6 position).



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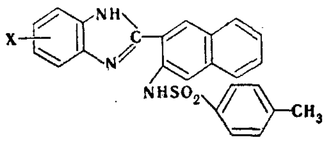

II

The optical characteristics of these compounds are presented in Table 1.

In analogy with the above-mentioned o-tosylamino-substituted 2-arylbenzoxazoles, one may assume the presence of an intramolecular hydrogen bond in the series of compounds that we investigated.

The absorption spectra of I had two maxima at 300-340 nm, and the shortwave band [λ_{max} 300 nm (ε 12,000)] is similar with respect to its position and structure to the absorption

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