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FIRST REPRESENTATIVE OF MACROHETEROCYCLIC LIGANDS OF THE DIBENZO-[c,m]DIPYRAZOLO[3,4-f:4',3'-j][1,2,5,8,9,12]HEXAAZACYCLOTETRADECENE CLASS

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UDC 547.773'778.4'898.07:541.572.54:543.422'51

The first representative of macroheterocyclic ligands of the dibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]hexaazacyclotetradecene class was obtained by nontemplate cyclization of 4,4'-azobis(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) bis(methylsulfate) with 2,2'-diaminoazobenzene in an aprotic solvent in the presence of potassium carbonate or magnesium oxide.

Macroheterocyclic compounds of the 1,2,5,8,9,12-hexaazacyclotetradecene class have been obtained by the template method exclusively in the form of metal complexes [1] and are of practical interest [1-8]. The corresponding metal-free ligands have not been isolated despite the diversity of demetallization methods that have been used [1].

In the present research we were able to realize the nontemplate synthesis of a free ligand of the type under consideration by using a component with increased reactivity. Instead of 4,4'-azobis(5-chloro-3-methyl-1-phenyl-1H-pyrazole) (I, $R^1 = R^2 = Cl$) [9] we used the corresponding bispyrazolium salt, viz., 4,4'-azobis(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) bis(methylsulfate) (II), in nucleophilic substitution with 2,2'-diaminoazobenzene (IV).

All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances, Moscow 107370. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 239-243, February, 1984. Original article submitted April 29, 1983.

0009-3122/84/2002-0196$08.50

TABLE 1. IR and UV Spectra of III, V, and VI

Compound	c, mole/liter	ν, cm^{-1} (ε, liters-mole^{-1}-cm^{-1}), in CCl_4: CH_3, sym	CH_3, asym	CH, arom.	NH	NH_2, sym	NH_2, asym	λ_{max}, nm (in hexane) (log ε)
III*	$4{,}1\cdot10^{-4}$	2864 (182), 2876 (156)	2935 (307), 2965 (261)	3040 i (72), 3055 (75)	3259 (56) 3413 (18)			450 (4,56), 398 sh (4,19), 331 (4,17), 277 i (4,32), 254 sh (4,52), 230 sh (4,67)
	$4{,}0\cdot10^{-2}$	2863 (211), 2875 (185)	2930 (367), 2960 (336)	3034 (114), 3050 (108), 3060 i (98)	3255 (70), 3415 (14)			
V	$4{,}7\cdot10^{-4}$	2859 (45), 2874 sh (32)	2930 (124), 2962 (62), 2991 (38)	3042 i (41), 3054 (59), 3079 (72)	3229 (37) 3315 (33)			503 i (3,34), 409 sh (4,29), 384 (4,38), 328 (4,32), 304 (4,36), 255 (4,32), 227 (4,43)
	$3{,}9\cdot10^{-2}$	2858 (60), 2876 (49)	2930 (138), 2963 (82), 2991 (61)	3040 i (72), 3052 (88), 3077 (97)	3226 (45) 3316 (29)			
VI	$4{,}0\cdot10^{-4}$	2861 (56), 2877 (49)	2931 (127), 2966 (99), 2985 i (43)	3060 sh (55), 3080 (67)	3320 (18)	3405 (24)	3493 (64)	463 i (4,10), 403 i (4,35), 382 (4,39), 333 (4,45), 252 i (4,43), 229 (4,56)
	$4{,}1\cdot10^{-2}$	2860 (68), 2876 (62)	2931 (153), 2964 (114), 2983 sh (62)	3055 sh (84), 3078 (90)	3320 (18)	3405 (19)	3494 (53)	

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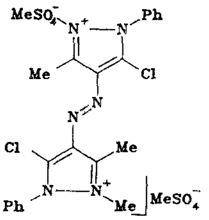
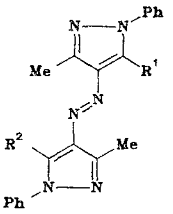
*In the case of III the νCH_3 bands are overlapped with the absorption bands of the C_4H_9 substituents.

An increase in the lability of a halogen atom in the pyrazole ring in nucleophilic substitution reactions under the influence of quaternization [10, 11] or when there is an azo group in the ortho position relative to a halogen atom [12] was previously observed by Michaelis and co-workers. We used both of these effects simultaneously.

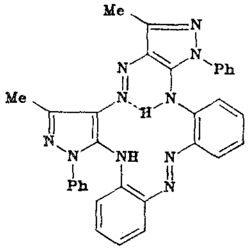
Bisquaternized derivative II was obtained by the reaction of I with dimethyl sulfate. When we carried out nucleophilic substitution of the chlorine atoms by a (4-butylphenyl)-amino group we established that replacement of the halogen atoms in I does not occur even upon prolonged heating; replacement occurs rapidly in II to give 4,4'-azobis[5-(4-butylanilino)-3-methyl-1-phenyl-1H-pyrazole] (III, $R^1 = R^2 = NHC_6H_4Bu$-p) and I. The phenomenon of dealkylation for quaternized alkylaryl-substituted pyrazoles was noted by Michaelis and co-workers [10, 11, 13] and others [14, 15].



II



I, III, VI



V

I $R^1=R^2=Cl$; III $R^1=R^2=NHC_6H_4Bu$-p; VI $R^1=Cl$; $R^2=NHC_6H_4(N_2C_6H_4NH_2$-o)-o

Bands of stretching vibrations of free and associated NH groups at 3413 and 3259 cm^{-1}, respectively, are observed in the IR spectrum of a $4.8\cdot10^{-4}$ mole/liter of III in CCl_4 (Table 1). When the concentration is increased to $3.9\cdot10^{-2}$ mole/liter, the intensity of the band at 3413 cm^{-1} decreases, as expected, but the intensity of not only the band at 3259 cm^{-1} but also the intensities of the bands of the stretching vibrations of aromatic and aliphatic CH groups at 2800-3100 cm^{-1} increase. The latter evidently indicates the presence at 2800-3200 cm^{-1} of a very broad band of absorption of NH groups tied up in an intermolecular hydrogen bond and its increasing contribution as the concentration is increased. On the basis of this the band at 3259 cm^{-1} can be assigned to an NH group tied up in an intramolecular hydrogen bond, and the other is either free or participates in an intermolecular bond (see Table 1).

One signal of NH protons and magnetic equivalence of the protons of the two parts of the molecule separated by an azo bond are observed in the PMR spectra of III (Table 2) in

TABLE 2. PMR Spectra of III, V, and VI (in $CDCl_3$, ppm)

Compound	Pyrazole ring			Benzene ring
	3-CH_3	5-NH(NH_2)	N—Ph	
III	2,42 (s 6H)	8,60 (s 2H)	7,33 (m 4H); 7,02 (m 6H)	6,46 (d 4H; 2,6,2′,6′-H), 6,70 (d 4H, 3,5,3′,5′-H); 2,33 (t 4H); 1,46—1,00 (m 8H), 0,80 (t 6H)
V	2,48 (s 6H)	10,97 (s 1H) 11,78 (s 1H)	~7,12 (8H), 6,76 (2H)	6,35 (m 2H), 6,76 (4H), 7,64 (2H)
VI	2,35 (s 3H) 2,59 (s 3H)	5,60 (s 2H); 10,10 (s 1H)	6,64—7,71 (m 18H)	

solutions in CCl_4, $CDCl_3$, and d_6-DMSO as a result of proton exchange. The slight changes in the chemical shift of the NH proton on passing from a solution in CCl_4 to a solution in d_6-DMSO ($\Delta\delta$ = 0.18 ppm at $3 \cdot 10^{-2}$ mole/liter) and the slight concentration dependence of the chemical shifts of the NH protons in slightly polar solvents (for example, the chemical shift changes from 8.57 to 8.69 ppm in CCl_4 over the concentration range $1 \cdot 10^{-3}$ to $1.3 \cdot 10^{-1}$ mole/liter) are evidently explained by a random compensation of the factors that determine its value.

The increased reactivity of the halogen atoms in II was used in the nontemplate synthesis of a metal-free macroheterocyclic compound of the hexaazacyclotetradecene class. We used 2,2'-diaminoazobenzene (IV) as the nucleophilic reagent and carried out the reaction in a polar aprotic solvent (DMF) in the presence of potassium carbonate or magnesium oxide. We found that a macroheterocyclic compound, viz., 1,8,9,20-tetrahydro-3,6-dimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]hexaazacyclotetradecene (V), and a product of single nucleophilic substitution, viz., 5-{[2-(2-aminophenylazo)phenyl]amino}-4-[(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)azo]-3-methyl-1-phenyl-1H-pyrazole [VI, R^1 = Cl, R^2 = $NHC_6H_4(N_2C_6H_4NH_2\text{-}o)\text{-}o$], which was previously obtained by demetallation of the Ni(II) complex [9], are formed in the course of the synthesis. Compound I is formed as a result of side dealkyaltion.

The mass spectrum of V contains a molecular-ion peak (m/z 550), which is the most intense peak in the spectrum; the molecule contains neither halogen nor metal atoms. The fragmentation of V proceeds via two independent pathways that are typical for azo compounds, viz., fragmentation into two parts with the formation of fragment ions with m/z 275 (71.8%) and 276 (48.7%), which possibly have pyrazolotriazole structures [16], and cleavage of the N–N bond to give fragment ions with m/z 261 (48.8%) through the hydrazone form of the molecular ion. The IR spectra of V and VI in solutions have regular character (Table 1). The ~100 cm^{-1} low-frequency shift and the greater (by a factor of almost two) half width of the band at 3320 cm^{-1} in the IR spectrum of VI as compared with the absorption band of the free NH group in III, as well as the absence of a concentration dependence of the band at 3320 cm^{-1}, make it possible to assign it with confidence to an NH group tied up in an intramolecular hydrogen bond. A decrease in the intensity of the free bands in the NH_2 group and an increase (but to a lesser extent than for III) in the background absorption at 2800-3200 cm^{-1} due to the absorption of NH_2 groups tied up in an intermolecular hydrogen bond are observed in the spectrum of VI when the concentration is increased to $4 \cdot 10^{-2}$ mole/liter. In the PMR spectrum of VI in solution in d_6-DMSO the signal of the NH proton is shifted 0.65 ppm to stronger field as compared with the spectrum of a solution in $CDCl_3$. The highest-frequency band in the IR spectrum of V coincides in position with the band of the NH group tied up in an intramolecular hydrogen bond in VI. However, the absence of the characteristic broadening of this band and the decrease in its intensity as the concentration is increased mean that this is the band of free NH groups. The significant low-frequency shift of this band in the spectrum of V as compared with the spectrum of III is evidently due to the electronic and steric factors that arise in the formation of a macroring. As in the case of the III concentration, when the concentration of macroring V is increased to ~$4 \cdot 10^{-2}$ mole/liter, the ε values of all of the bands at 2800-3250 cm^{-1} increase; this is due to an increase in the very broad band (or bands) of the NH groups tied up in an intermolecular bond.

The closeness of the form and position of the bands at 3235 and 3258 cm^{-1} in the spectra of V and III also suggests their identical assignment to an NH group tied up in an intramolecular hydrogen bond with the N atom of the azo group of the azopyrazole fragment, since only this type of intramolecular hydrogen bond is possible in III. However, judging from the markedly differing character of the band, the alternative possibility of the formation of an intramolecular hydrogen bond with the N atom of the azo group of the azobenzene fragment is realized in VI but not in V. The presence in the V macroring of two types of NH groups, viz., an NH group tied up in an intramolecular hydrogen bond and a free (or partially intermolecularly bonded) NH group, is confirmed by the PMR spectra of solutions in $CDCl_3$, in which one observed signals of protons of both NH groups, viz., an intramolecularly bonded NH group at 11.78 ppm and a free NH group at 10.97 ppm. As in the case of III, one observed one signal of NH protons at 10.76 ppm in the spectrum of a solution of V in d_6-DMSO. Significant exchange broadening of the signals of the aromatic protons, which indicates the conformational lability of the hexaazatetradecene skeleton of the macroring, is also noted in the spectra. A consequence of this lability and, in addition, the noncoplanarity of the hexaazatetradecene skeleton in V is, on the one hand, the inability of one of the NH groups to form an intramolecular hydrogen bond and, on the other, its ability to form an intermolecular bond. The noncoplanarity of the V molecule is also confirmed by the electronic absorption spectra, which, as is apparent from Table 1, are similar for V and VI, except for the 38-nm bathochromic shift of the longest-wave transition in V. The absence of an appreciable increase in the intensity in the electronic absorption spectrum on passing from VI to V indicates that V is not a unified conjugation system [17]. It is apparent that the azobenzene fragment in V is not coplanar with the azopyrazole fragment, the planarity of which is stabilized by an intramolecular hydrogen bond.

EXPERIMENTAL

The purity of the compounds obtained was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates and by elementary analysis. The PMR spectra were obtained with a Varian XL-100 spectrometer with tetramethylsilane as the internal standard. The IR spectra of solutions in $CHCl_3$ and CCl_4 and of KBr pellets were recorded with UR-20 and Specord IR-75 spectrometers. The electronic absorption spectra were obtained with a Specord UV-vis spectrophotometer. The mass spectra were recorded with an MS-702 mass spectrometer with direct introduction of the samples into the ionization region; the ionizing-electron energy was 70 eV, and the temperature of the system for vaporization of the samples was 180-200°C.

4,4'-Azobis(5-chloro-3-methyl-1-phenyl-1H-pyrazole) (I) was obtained by the method in [9]; a product with mp 227-228°C (mp 226°C [13]) was obtained in 45% yield.

4,4'-Azobis(5-chloro-2,3-dimethyl-1-phenyl-1H-pyrazolium) Bis(methylsulfate) (II). A 4.11-g (0.01 mole) sample of pyrazole I was heated and stirred at 130-140°C in 70 ml of dry m-xylene or chlorobenzene. After I had dissolved, 3.0 g (0.023 mole) of dimethyl sulfate was added dropwise in the course of 5 min, and the mixture was maintained at the indicated temperature for 3 h. It was then cooled, and the crystalline precipitate was removed by filtration to give 6.27 g (90%) of yellow crystals of salt II (dec. at 239°C) that were quite soluble in water, methanol, and ethanol but insoluble in hexane, heptane, chloroform, benzene, toluene, DMF, and DMSO. PMR spectrum (in D_2O): 7.68-7.98 (10H, m, N—Ph), 3.88 (6H, s, N—CH_3), 3.70 (6H, s, $CH_3OSO_3^-$), and 2.91 ppm (6H, s, 3-CH_3). IR spectrum (KBr): 3093, 3042, 3030 (CH); 2963 (CH_3); 2854 (CH_3); 1616, 1593, 1553, 1515, 1503, 1465, 1454 (C=C, C=N, N=N); 1255 (O—CH_3); 1220 (SO_3^-); 1031 (SO_3^-); 762 cm^{-1} (CH—NPh). UV spectrum (in alcohol), λ_{max} (log ε): 422 (3.28), 413 (3.28), 332 sh (4.27), 320 (4.38), 312 sh (4.32), and 226 nm (4.29). Found: C 43.6; H 4.3; Cl 10.7; N 12.7; S 9.5%. $C_{24}H_{28}Cl_2N_6O_8S_2$. Calculated: C 43.4; H 4.2; Cl 10.7; N 12.7; S 9.7%.

4,4'-Azobis[5-(4-butylanilino)-3-methyl-1-phenyl-1H-pyrazole] (III). A mixture of 6.63 g (0.01 mole) of salt II, 2.99 g (0.02 mole) of n-butylaniline, and 5.50 g (0.04 mole) of K_2CO_3 in 70 ml of DMF was heated with stirring at 130-140°C for 6 h, after which the mixture was cooled, and the precipitate was removed by filtration and washed with 10 ml of DMF. The filtrates were combined, and the solvent was removed by distillation in vacuo. The residue was dissolved in 100 ml of benzene, and the solution was chromatographed with a column packed with SiO_2 by elution with benzene. The orange zone was collected and recrystallized from n-heptane to give 4.97 g (78.1%) of bright-orange needles of pyrazole III, which were quite soluble in many organic solvents and had mp 151-152°C and R_f 0.18 (in chloroform). Found: C 75.4; H 6.9; N 17.4%. $C_{40}H_{44}N_8$. Calculated: C 75.5; H 7.0; N 17.6%.

1,8,9,20-Tetrahydro-3,6-dimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[5,4-f:4',5'-j]-[1,2,5,8,9,12]hexaazacyclotetradecene (V). A) A mixture of 0.66 g (0.001 mole) of salt II, 0.21 g (0.001 mole) of IV, and 0.55 g (0.004 mole) of K_2CO_3 in 8.0 ml of DMF was heated with stirring to 130-140°C for 7-8 h, after which the mixture was cooled, and the precipitate was removed by filtration and washed with 2-3 ml of DMF. The solvent was removed from the combined filtrates by distillation in vacuo, and the residue was dissolved in 100 ml of benzene and chromatographed on SiO_2 by elution with benzene. The dark-brown zone was collected and recrystallized from dry acetone to give 0.10 g (20.1%) of red-brown crystals of macrocycle V, which were quite soluble in benzene, toluene, and chloroform, less soluble in hexane, heptane, and acetone, and insoluble in alcohols and had mp 265-266°C and R_f 0.14 (in chloroform). Found: C 69.9; H 4.8; N 25.3%; M^+ 550. $C_{32}H_{26}N_{10}$. Calculated: C 69.8; H 4.8; N 25.4%; M 550.

B) Instead of the K_2CO_3 in method A, 0.08 g (0.002 mole) of MgO was used, and the mixture was heated for 5-6 h. Workup gave 0.14-0.16 g (25-30%) of product.

5-{[2-(2-Aminophenylazo)phenyl]amino}-4-[(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-azo]-3-methyl-1-phenyl-1H-pyrazole (VI). This compound was obtained in the synthesis of V. The first red-orange zone was collected, the solvent was removed by distillation, and the residual substance was recrystallized from ethanol to give 0.07 g (12%) of red-orange crystals with mp 118-119°C; the crystals were soluble in chloroform, acetone, and ethanol. Found: C 65.6; H 4.7; Cl 6.2; N 23.9%. $C_{32}H_{27}ClN_{10}$. Calculated: C 65.5; H 4.6; Cl 6.0; N 23.9%.

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